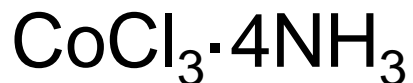
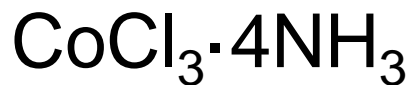
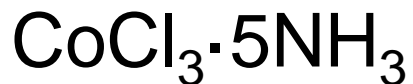
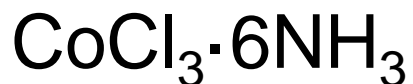




Alfred Werner 1866 – 1919
Premio Nobel per la chimica 1913

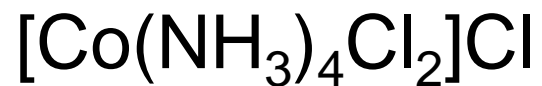
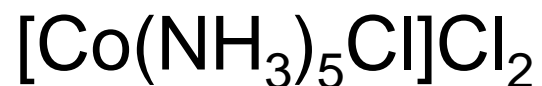
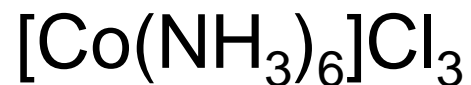


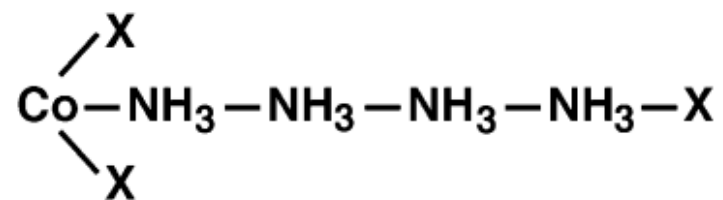
Giallo

Rosso-viola

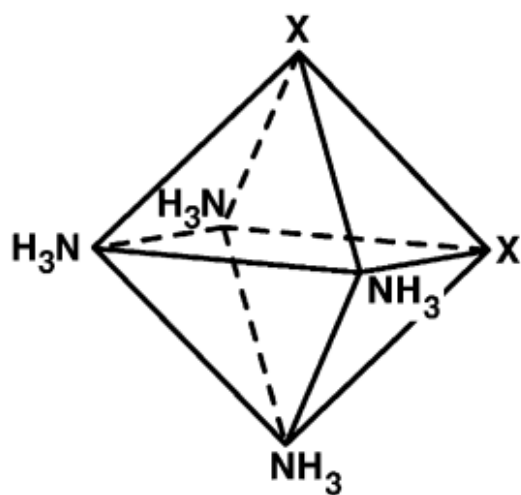
Verde

Violetto

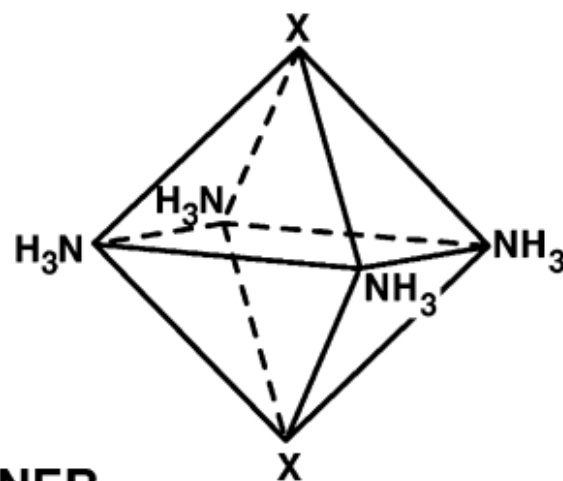


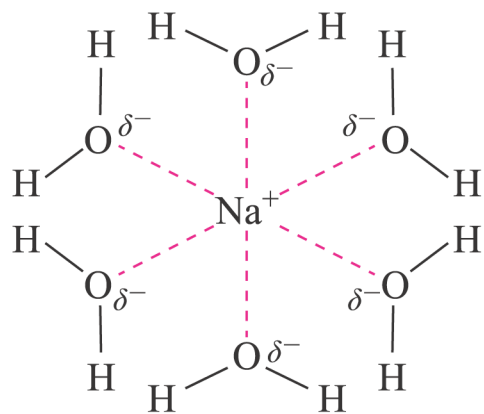


JØRGENSEN

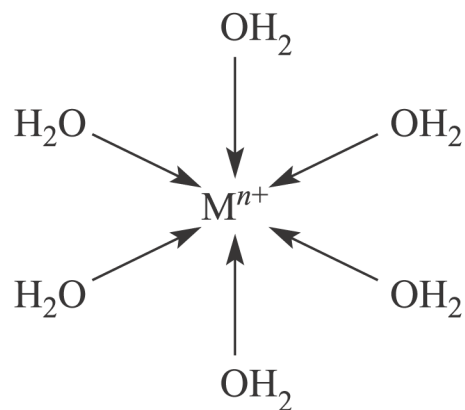
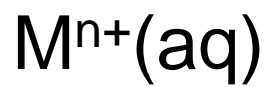


WERNER

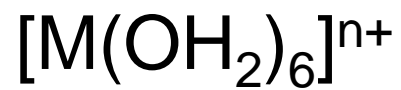




(a)

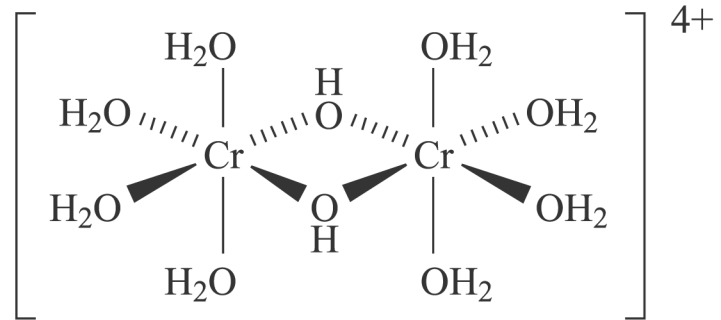


(b)

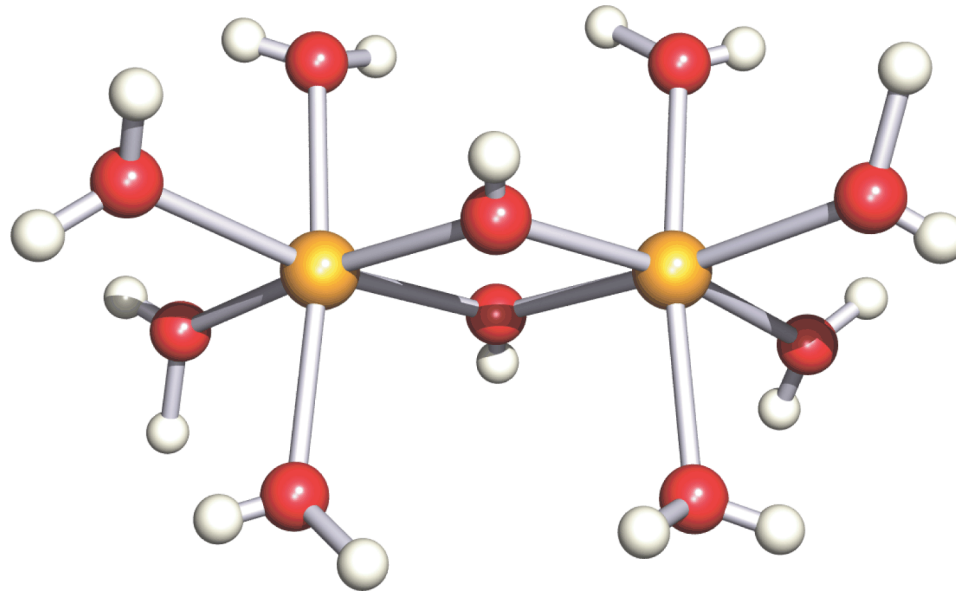


$$pK_a [\text{Fe}(\text{OH}_2)_6]^{3+}(\text{aq}) = 2.0$$

$$pK_a [\text{Fe}(\text{OH}_2)_5(\text{OH})]^{2+}(\text{aq}) = 3.3$$

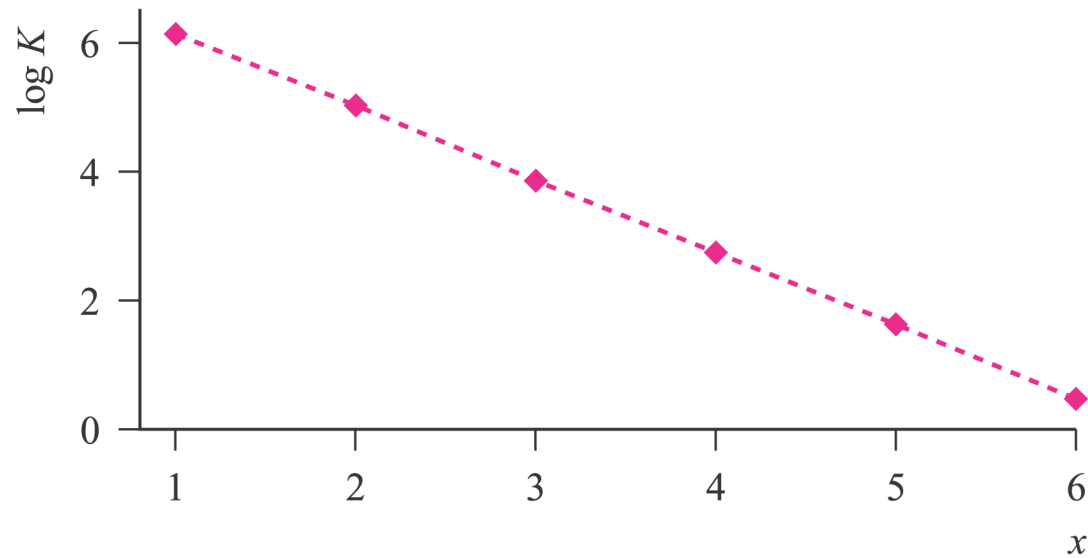


(a)

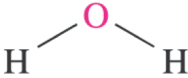
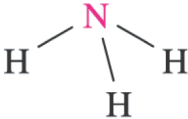

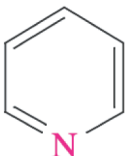



(b)

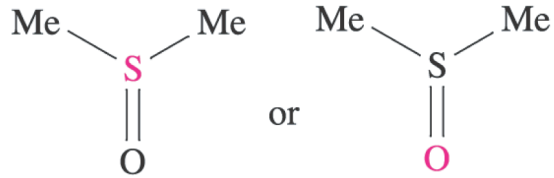
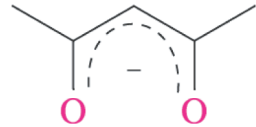
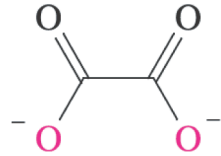
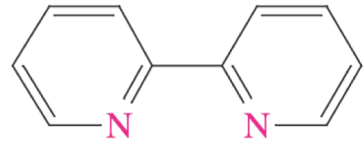
Costanti di stabilità parziali per la formazione di $[M(OH_2)_{6-x}L_x]^{n+}$

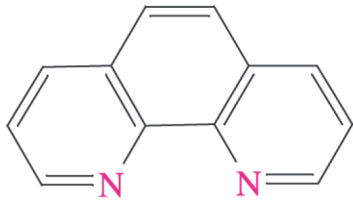




$$\beta = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6$$

| Name of ligand | Abbreviation (if any) | Denticity | Structure with donor atoms marked in red |
|--------------------------------|-----------------------|-------------|--|
| Water | | Monodentate |  |
| Ammonia | | Monodentate |  |
| Tetrahydrofuran | THF | Monodentate |  |
| Pyridine | py | Monodentate |  |
| 1,2-Ethanediamine [†] | en | Bidentate |  |

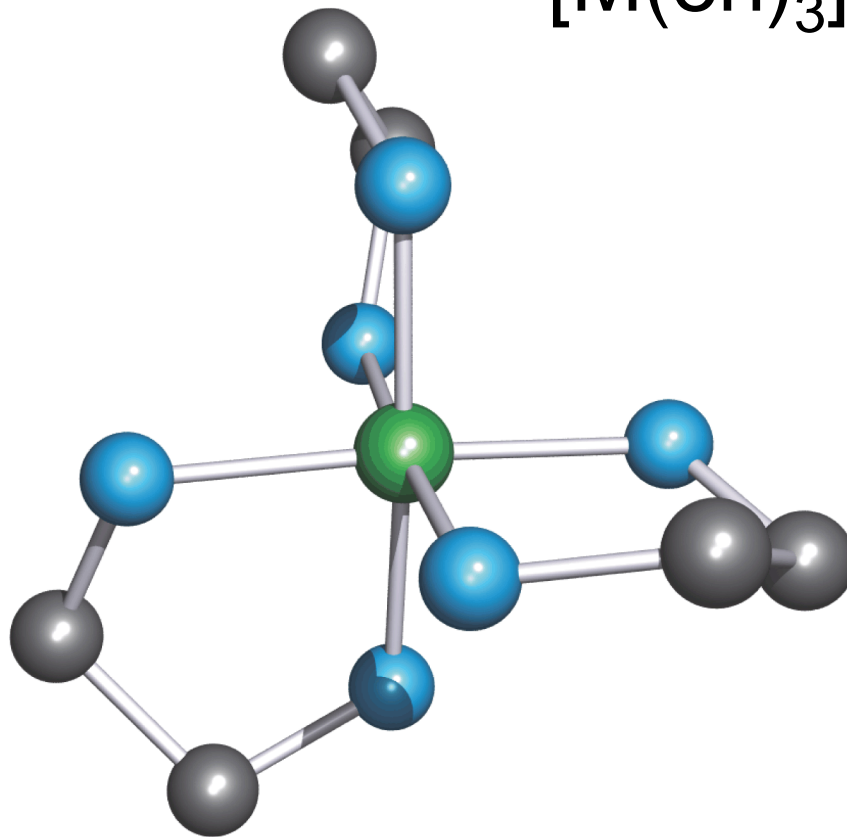
[†] The older names (still in use) for 1,2-ethanediamine, 1,4,7-triazaheptane and 1,4,7,10-tetraazadecane are ethylenediamine, diethylenetriamine and triethylenetetramine.

| Name of ligand | Abbreviation (if any) | Denticity | Structure with donor atoms marked in red |
|-----------------------------|-----------------------|-------------|---|
| Dimethylsulfoxide | DMSO | Monodentate |  |
| Acetylacetonate ion | [acac] ⁻ | Bidentate |  |
| Oxalate or ethanedioate ion | [ox] ²⁻ | Bidentate |  |
| 2,2'-Bipyridine | bpy or bipy | Bidentate |  |

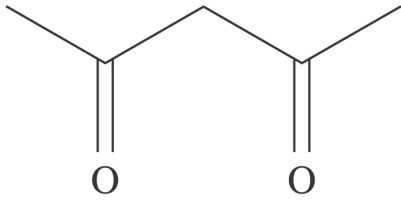
| Name of ligand | Abbreviation (if any) | Denticity | Structure with donor atoms marked in red |
|--|-----------------------|--------------|---|
| 1,10-Phenanthroline | phen | Bidentate |  |
| 1,4,7-Triazaheptane [†] | dien | Tridentate |  |
| 1,4,7,10-Tetraazadecane [†] | trien | Tetradentate |  |
| <i>N,N,N',N'</i> -Ethylenediaminetetraacetate ion [‡] | [EDTA] ⁴⁻ | Hexadentate | See equation 7.75 |

[†] The older names (still in use) for 1,2-ethanediamine, 1,4,7-triazaheptane and 1,4,7,10-tetraazadecane are ethylenediamine, diethylenetriamine and triethylenetetramine.

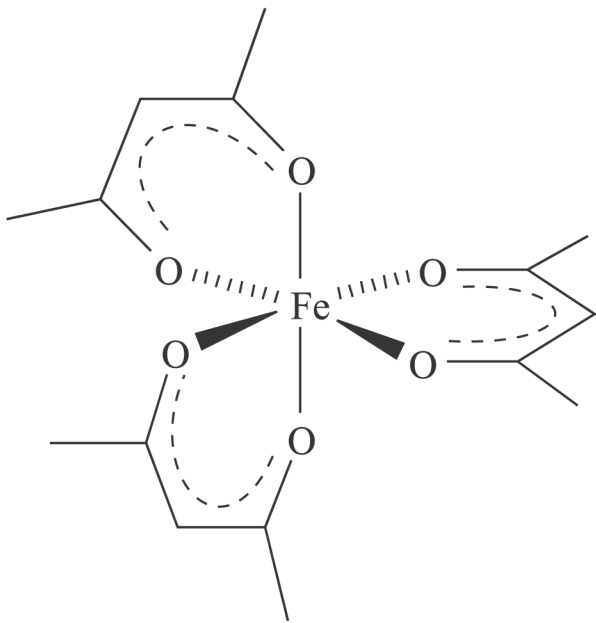
[‡] Although not systematic by the IUPAC rules, this is the commonly accepted name for this anion.



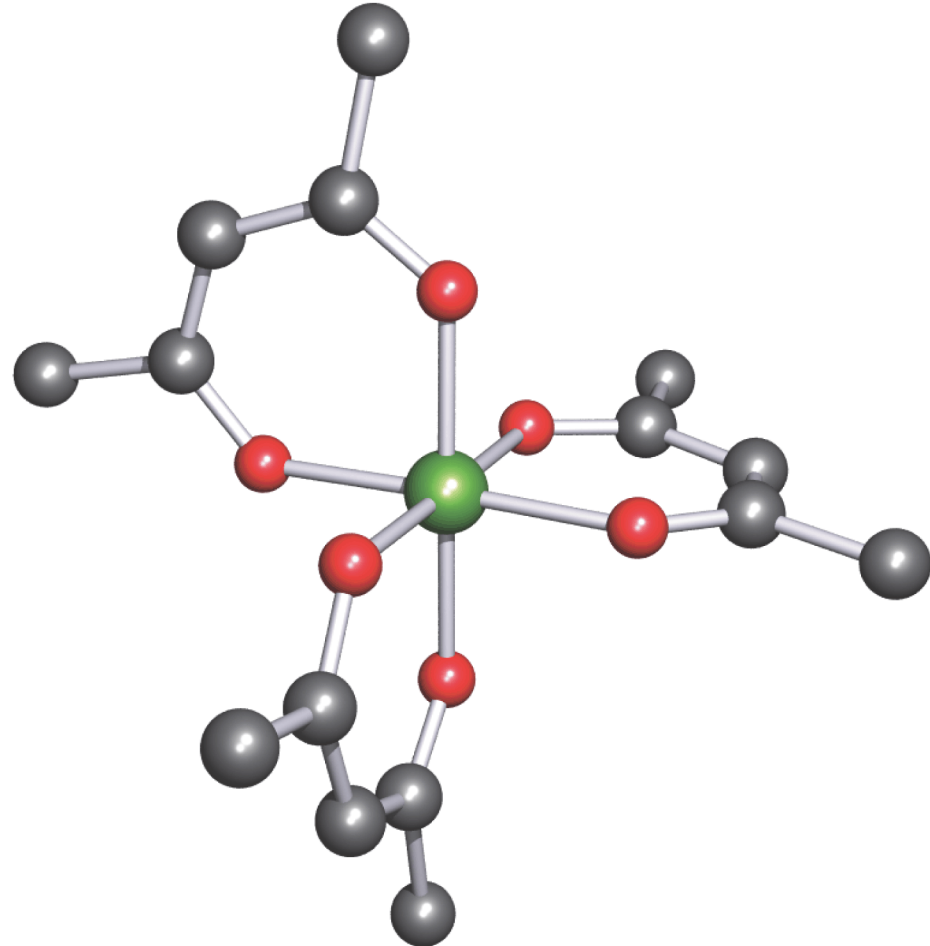
Anelli chelati a 5 termini



(a)

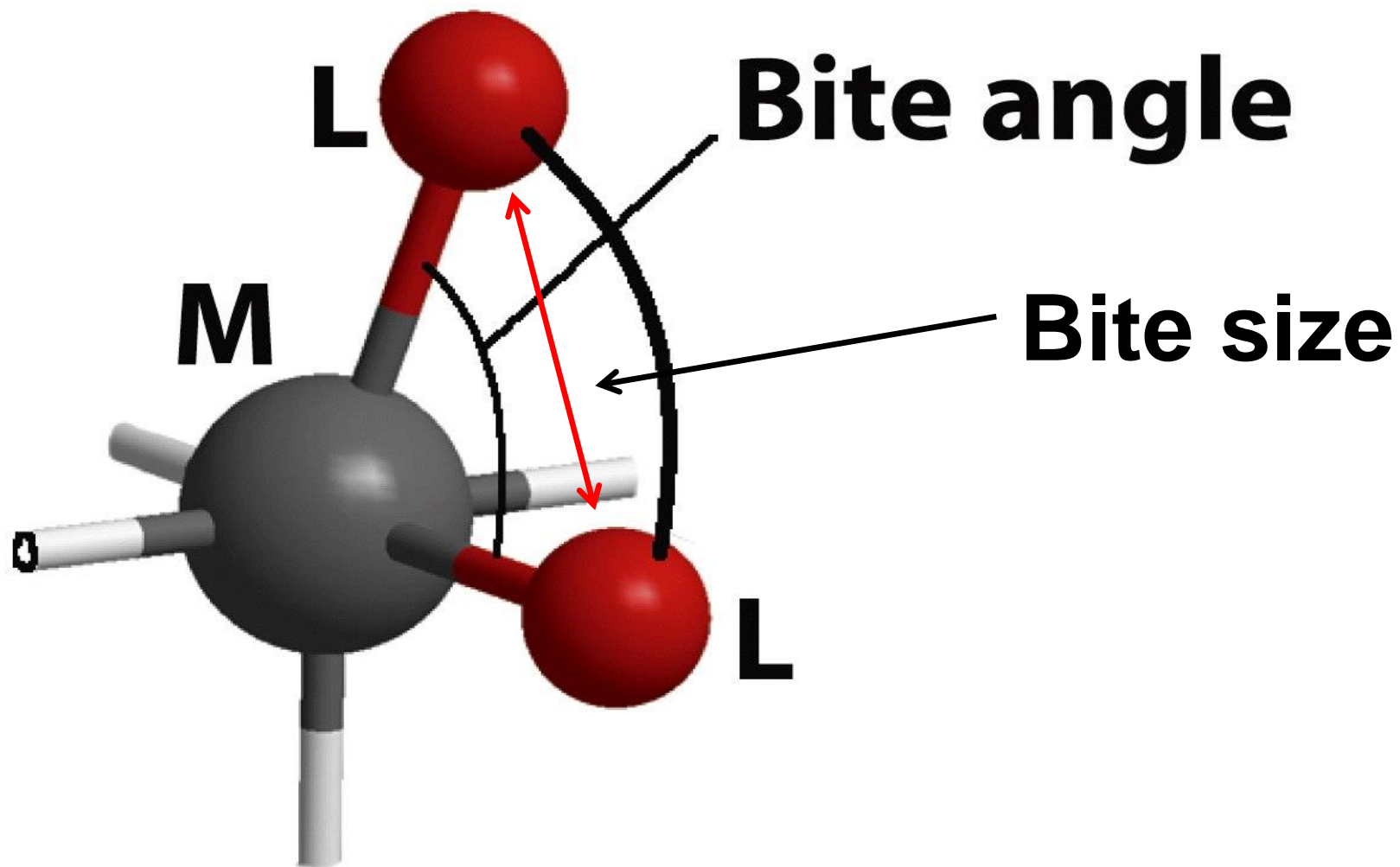


(b)

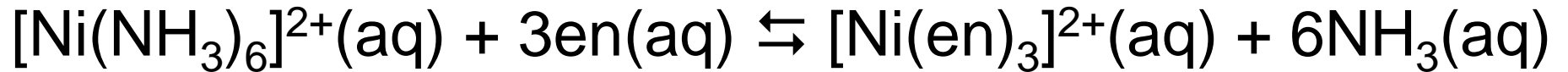


(c)

Anelli chelati a 6 termini



Effetto chelante



$$\log K = 9.27$$

$$\Delta G^\circ = -52.9 \text{ kJ mol}^{-1}$$

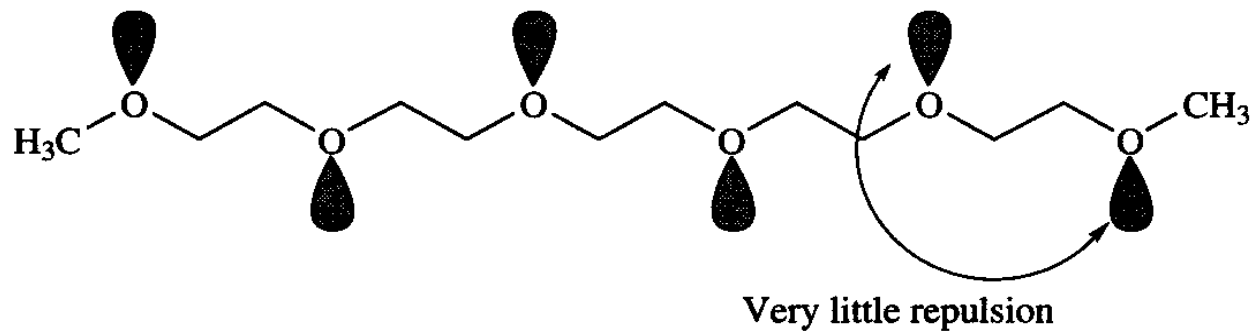
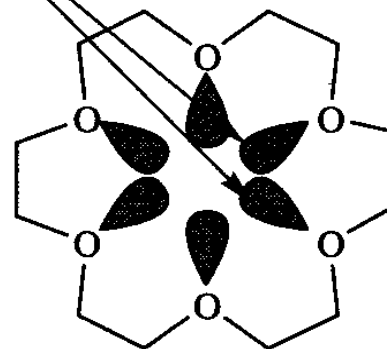
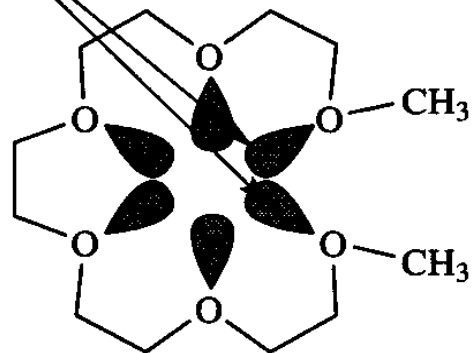
$$\Delta H^\circ = -16.8 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = +121 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T\Delta S^\circ = +31.6 \text{ kJ mol}^{-1}$$

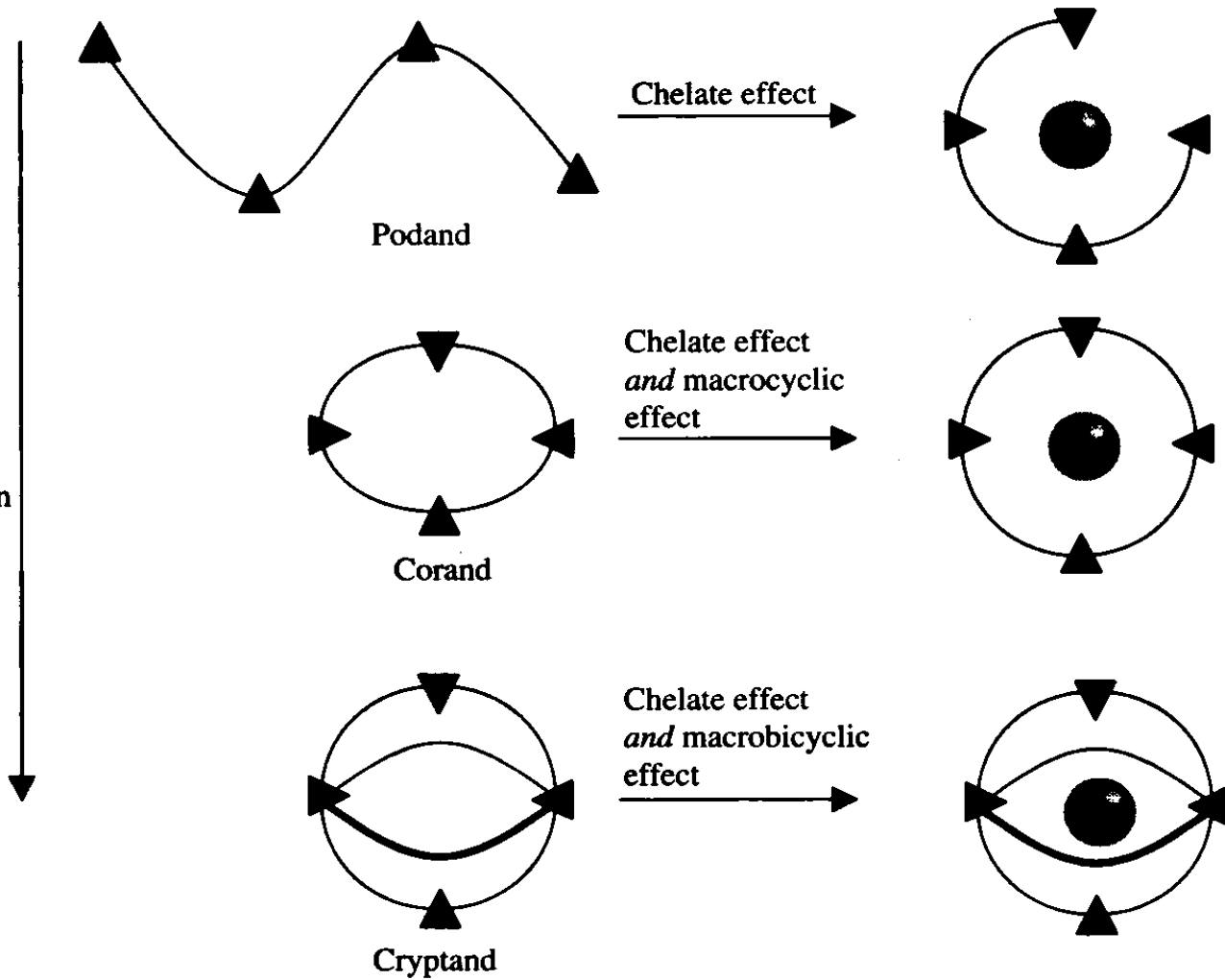
Effetto macrociclo

Lone pair-lone pair repulsive interaction



podando

Increasing
degree
of host
organisation



| | Metal ion | log K_1 | | | |
|----------|-----------------------|-----------|--------|--------|-------|
| | | X = F | X = Cl | X = Br | X = I |
| a | Fe ³⁺ (aq) | 6.0 | 1.4 | 0.5 | – |
| b | Hg ²⁺ (aq) | 1.0 | 6.7 | 8.9 | 12.9 |

F > O > N > Cl > Br > C ≈ I ≈ S > Se > P > As > Sb

Hard

Soft

F > Cl > Br > I

O » S > Se > Te

N » P > As > Sb

F < Cl < Br < I

O « S > Se ≈ Te

N « P > As > Sb

HSAB Principle

Metal centres (Lewis acids)

| | |
|-----------------|---|
| Hard; class (a) | Li^+ , Na^+ , K^+ , Rb^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Sn^{2+} , Mn^{2+} , Zn^{2+} , Al^{3+} , Ga^{3+} , In^{3+} , Sc^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , Y^{3+} , Th^{4+} , Pu^{4+} , Ti^{4+} , Zr^{4+} , $[\text{VO}]^{2+}$, $[\text{VO}_2]^+$ |
| Soft; class (b) | Zero oxidation state metal centres, Tl^+ , Cu^+ , Ag^+ , Au^+ , $[\text{Hg}_2]^{2+}$, Hg^{2+} , Cd^{2+} , Pd^{2+} , Pt^{2+} , Tl^{3+} |
| Intermediate | Pb^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Os^{2+} , Ru^{3+} , Rh^{3+} , Ir^{3+} |

HSAB Principle

Ligands (Lewis bases)

| | |
|-----------------|--|
| Hard; class (a) | F^- , Cl^- , H_2O , ROH , R_2O , $[OH]^-$, $[RO]^-$, $[RCO_2]^-$, $[CO_3]^{2-}$, $[NO_3]^-$, $[PO_4]^{3-}$, $[SO_4]^{2-}$, $[ClO_4]^-$, $[ox]^{2-}$, NH_3 , RNH_2 |
| Soft; class (b) | I^- , H^- , R^- , $[CN]^-$ (<i>C</i> -bound), CO (<i>C</i> -bound), RNC , RSH , R_2S , $[RS]^-$, $[SCN]^-$ (<i>S</i> -bound), R_3P , R_3As , R_3Sb , alkenes, arenes |
| Intermediate | Br^- , $[N_3]^-$, py , $[SCN]^-$ (<i>N</i> -bound), $ArNH_2$, $[NO_2]^-$, $[SO_3]^{2-}$ |
