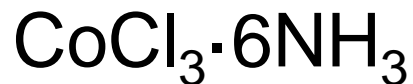


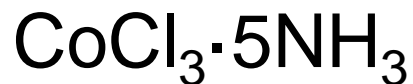
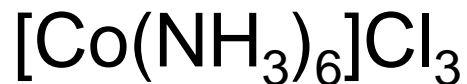
# Chimica di coordinazione



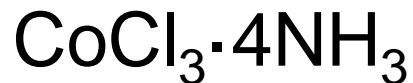
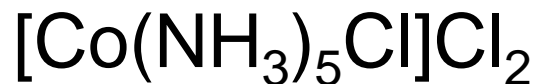
Alfred Werner 1866 – 1919  
Premio Nobel per la chimica 1913



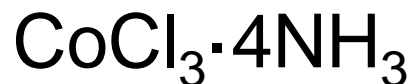
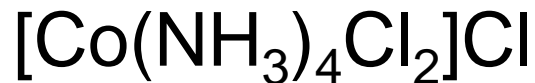
Giallo



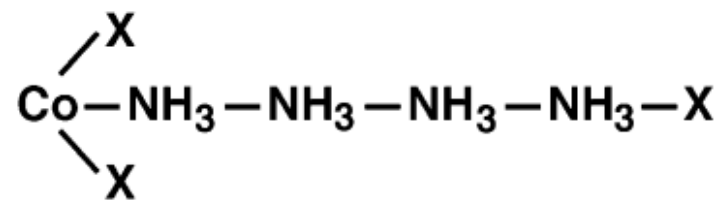
Rosso-viola



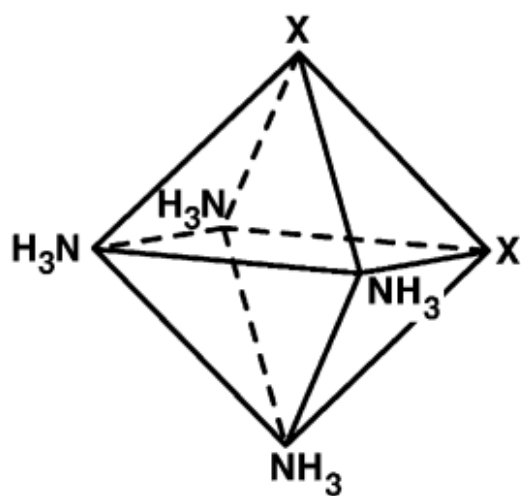
Verde



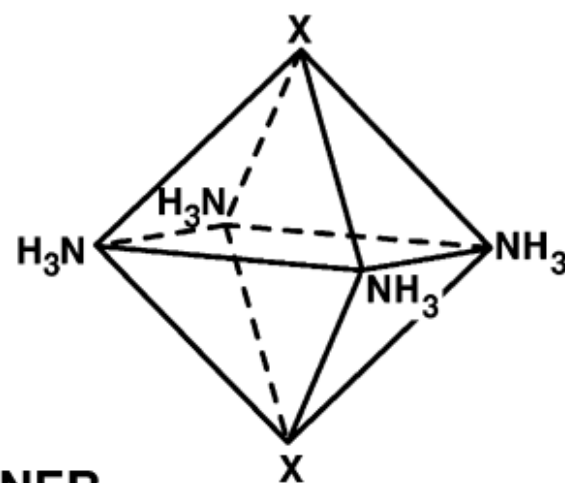
Violetto



**JØRGENSEN**



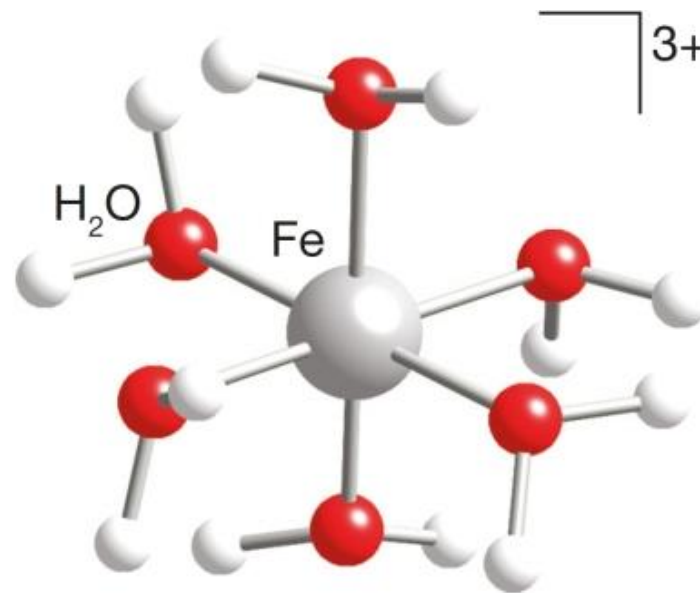
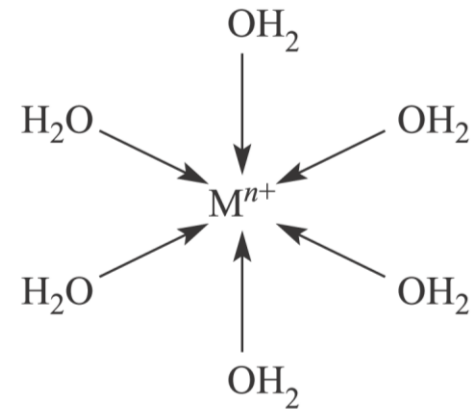
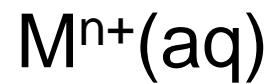
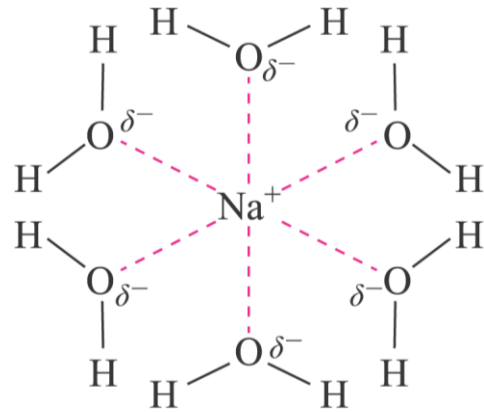
**WERNER**



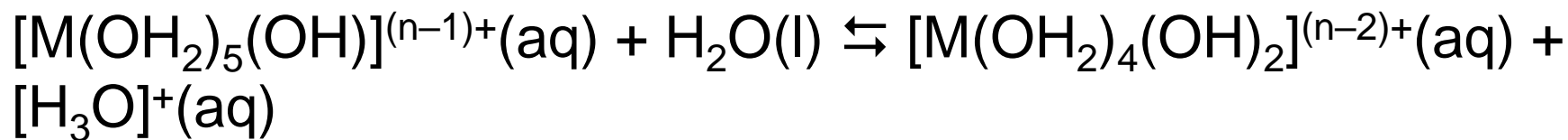
# Composti di coordinazione

In un composto di coordinazione (o complesso) un atomo (o ione) centrale è coordinato da molecole o ioni (solitamente tra 2 e 9) che si comportano sostanzialmente come **basi di Lewis** donando un doppietto elettronico all'atomo (o ione) centrale, che si comporta da **acido di Lewis**, formando **legami di coordinazione**. Gli atomi dei leganti che sono direttamente legati all'atomo (o ione) centrale sono detti **atomi donatori**. Il loro numero rappresenta il **numero di coordinazione**. L'insieme dei leganti si chiama anche la **sfera di coordinazione**.

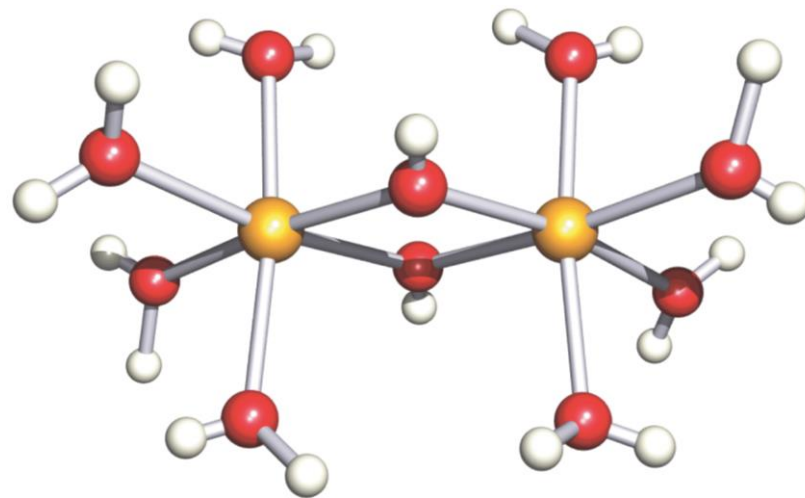
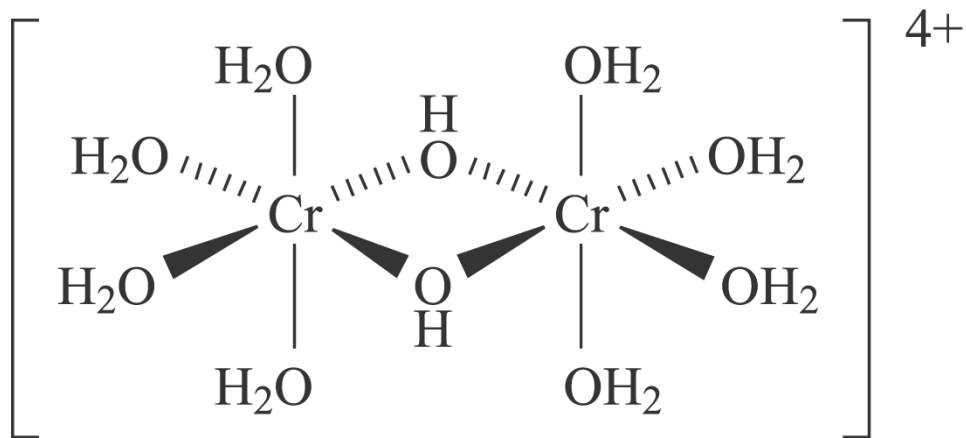
# Interazione elettrostatica o parzialmente covalente



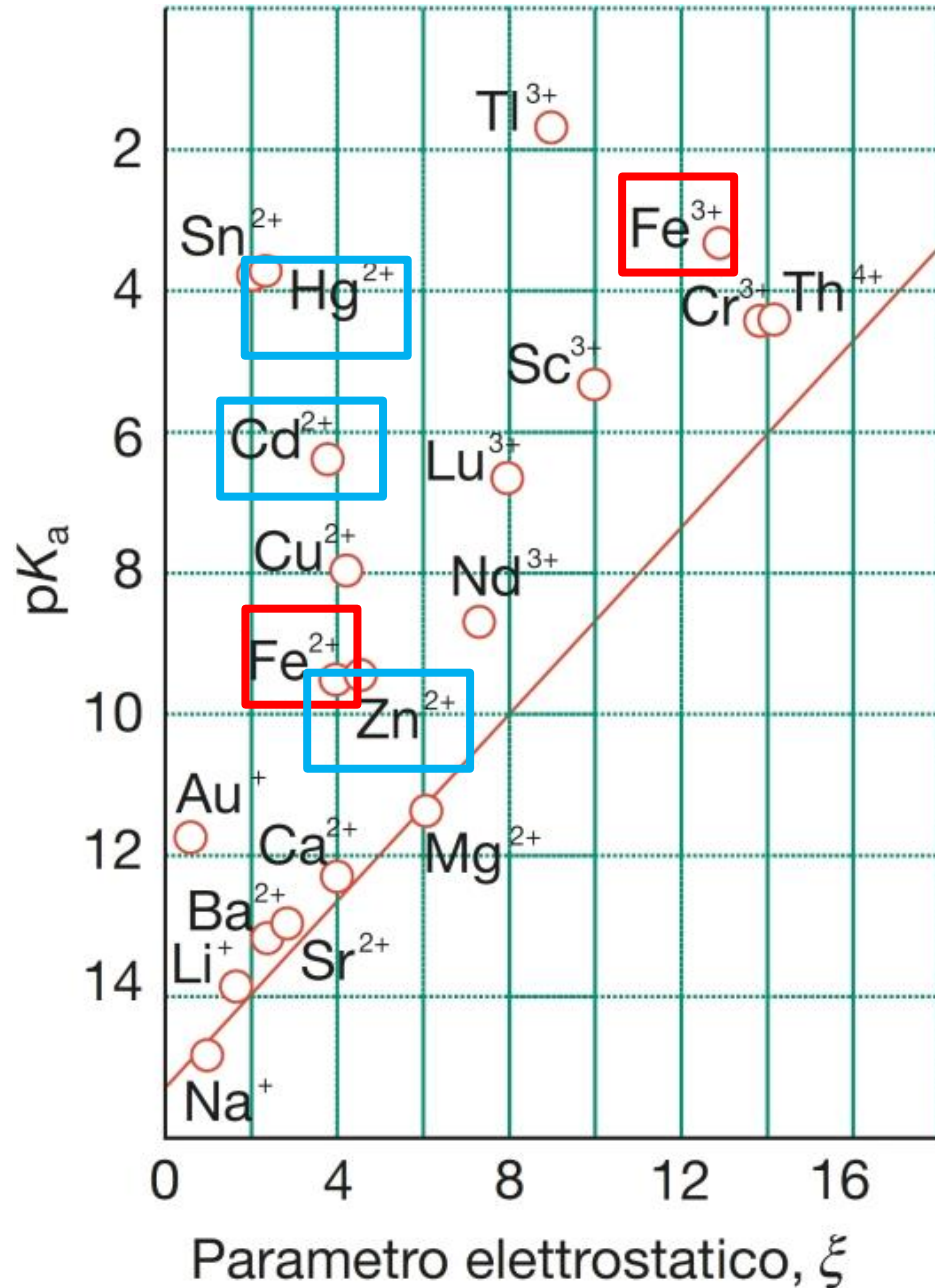
# Aquoacidi



$$pK_a [Fe(OH_2)_6]^{3+}(aq) = 2.0$$
$$pK_a [Fe(OH_2)_5(OH)_2]^{2+}(aq) = 3.3$$

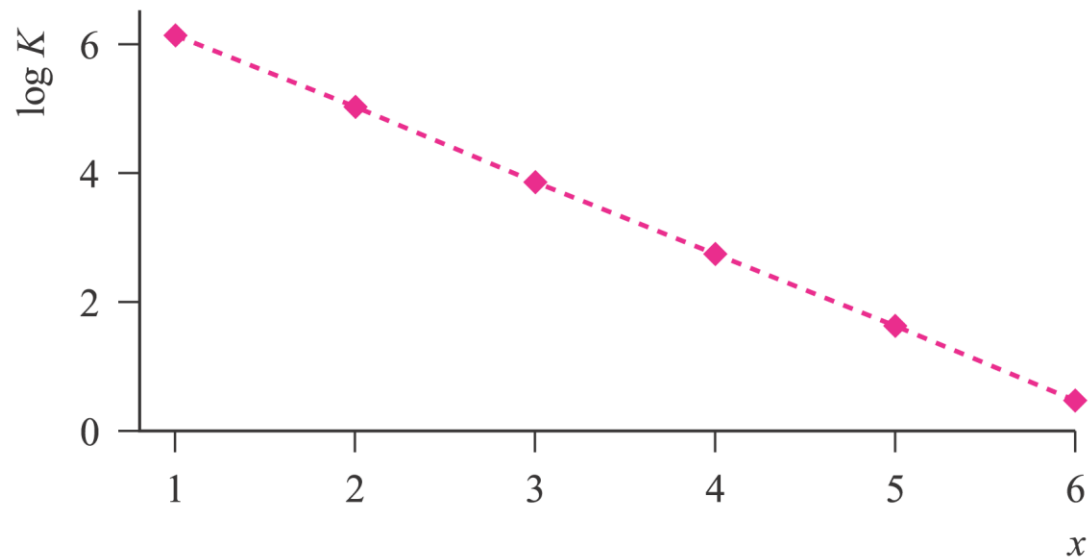


# Forza degli aquoacidi



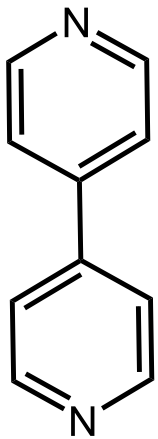
**FIGURA 5.4** La correlazione fra la costante di acidità  $pK_a$  e il parametro elettrostatico adimensionale  $\xi$  ( $= 100z^2/(r/\text{pm})$ ) per aquoioni. La retta indica l'andamento atteso in base al modello ionico.

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

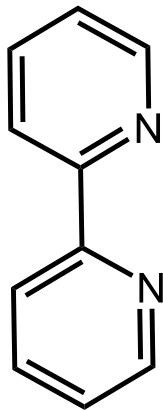


$$\beta = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6$$

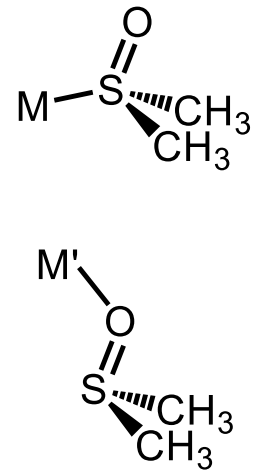
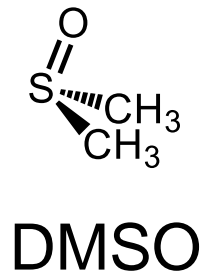
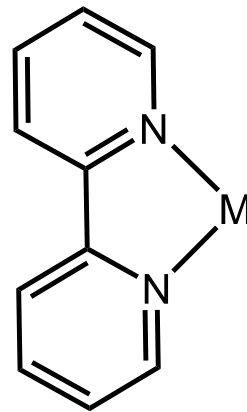
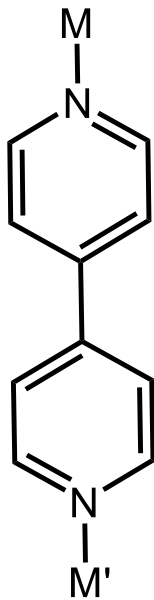
- Leganti politopici
- Leganti polidentati (chelanti)
- Leganti ambidentati



4,4'-bpy

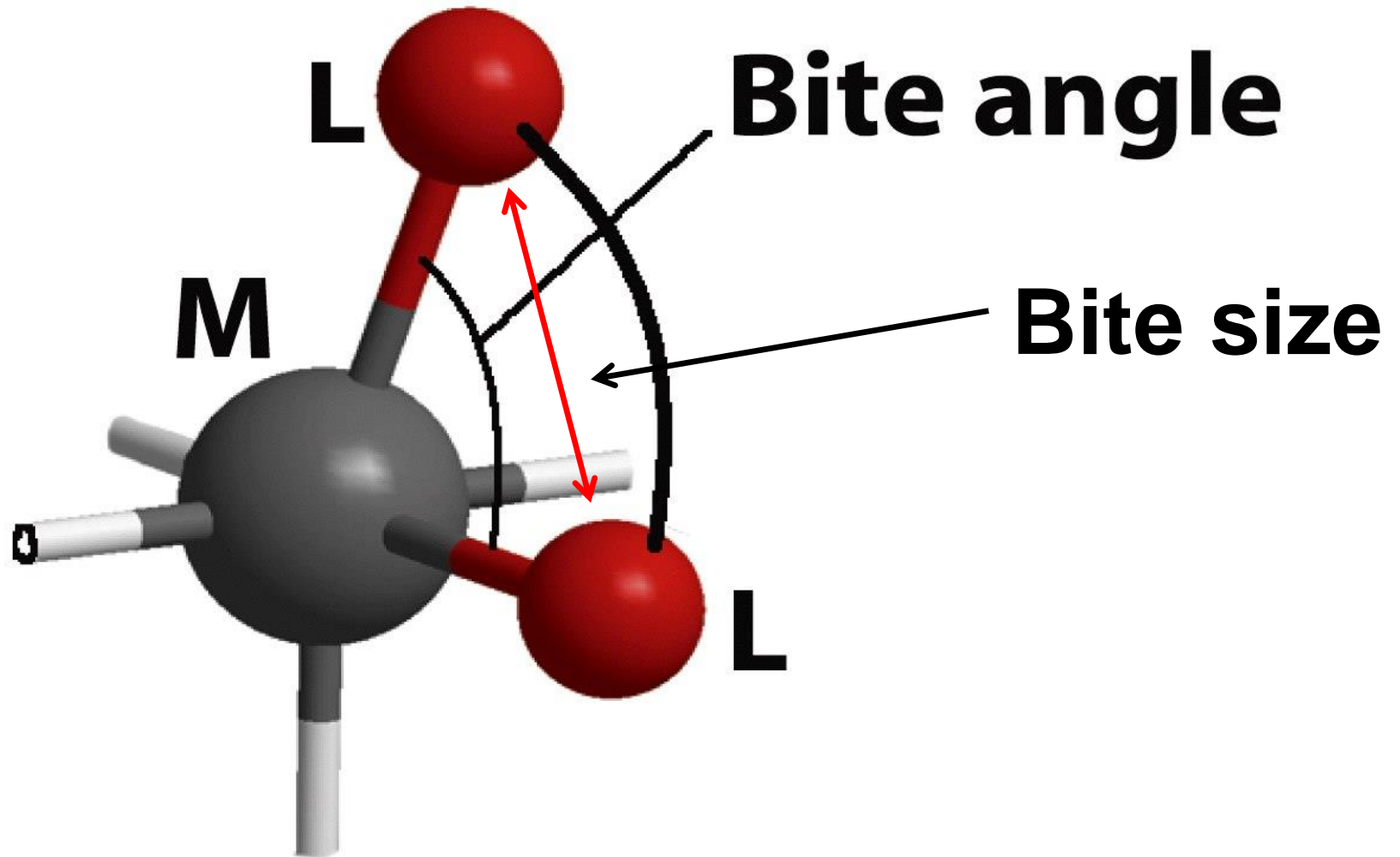


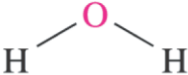
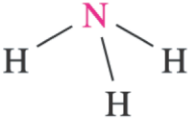

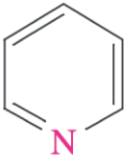

2,2'-bpy



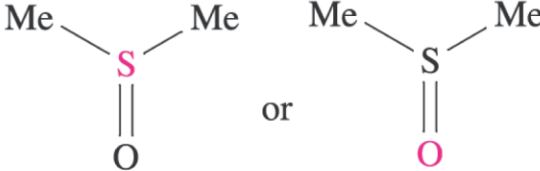
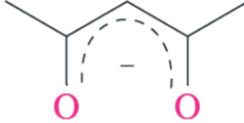
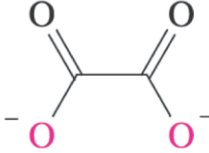
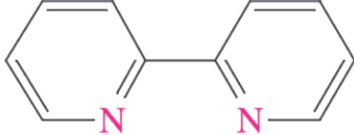


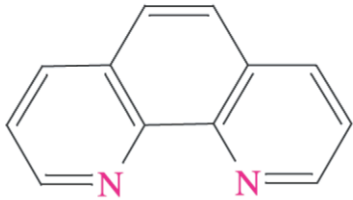


# Chelanti



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 <sup>†</sup>	en	Bidentate	

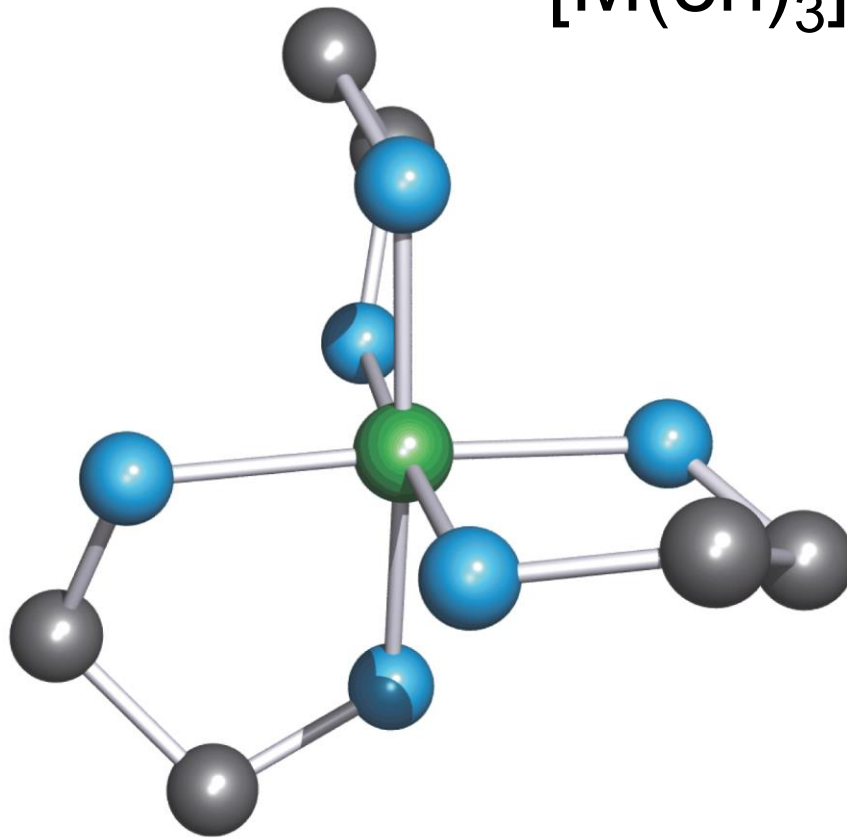
<sup>†</sup> The older names (still in use) for 1,2-ethanediamine, 1,4,7-triazaheptane and 1,4,7,10-tetraazadecane are ethylenediamine, diethylenetriamine and triethylenetetramine.

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

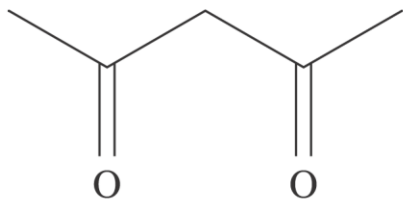
Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
1,10-Phenanthroline	phen	Bidentate	
1,4,7-Triazaheptane <sup>†</sup>	dien	Tridentate	
1,4,7,10-Tetraazadecane <sup>†</sup>	trien	Tetradentate	
<i>N,N,N',N'</i> -Ethylenediaminetetraacetate ion <sup>‡</sup>	[EDTA]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

<sup>†</sup> 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.

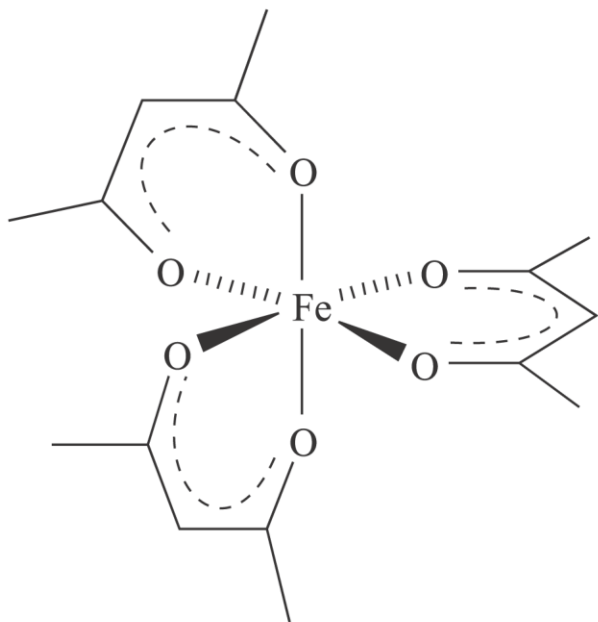
<sup>‡</sup> Although not systematic by the IUPAC rules, this is the commonly accepted name for this anion.



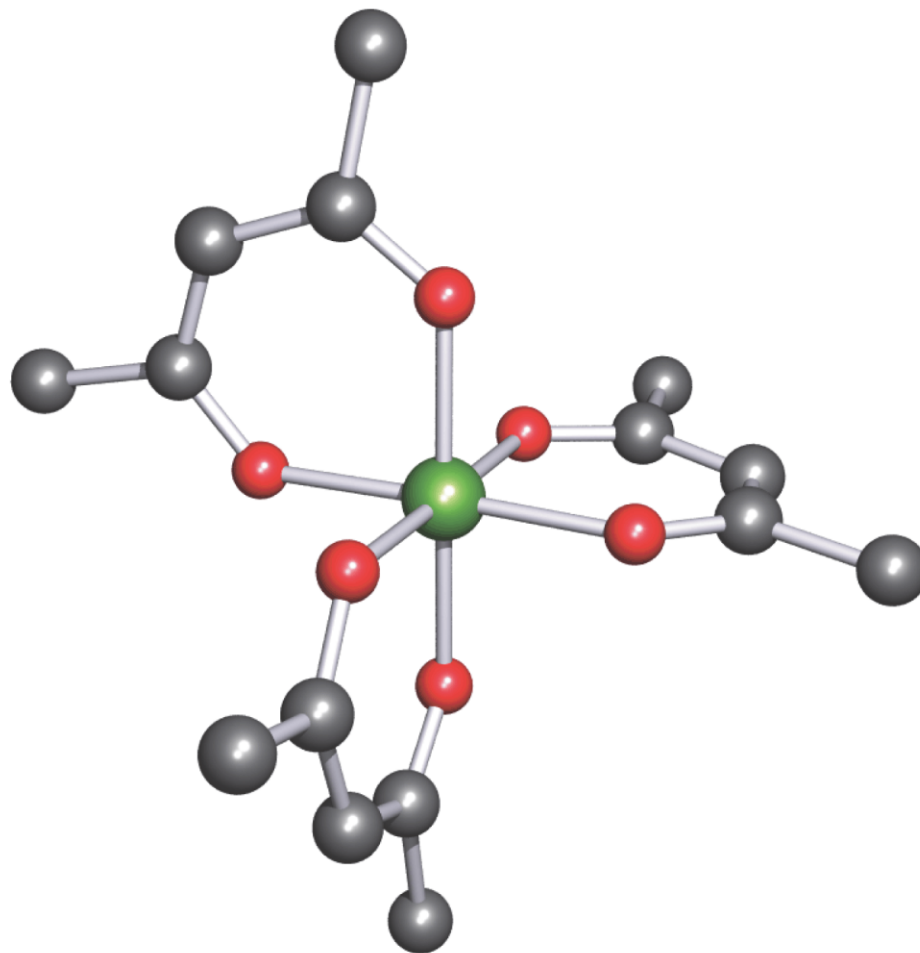
Anelli chelati a 5 termini



(a)



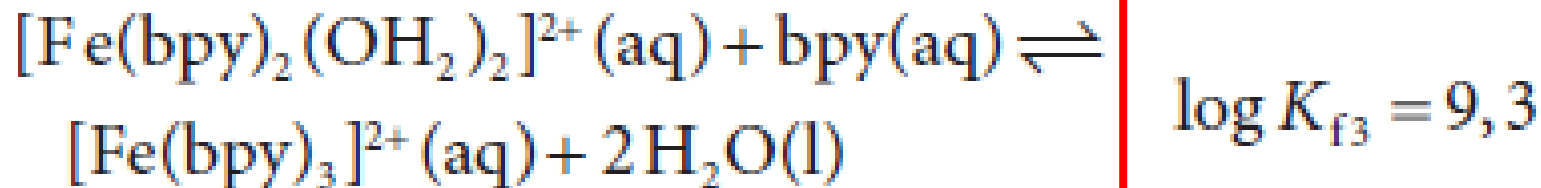
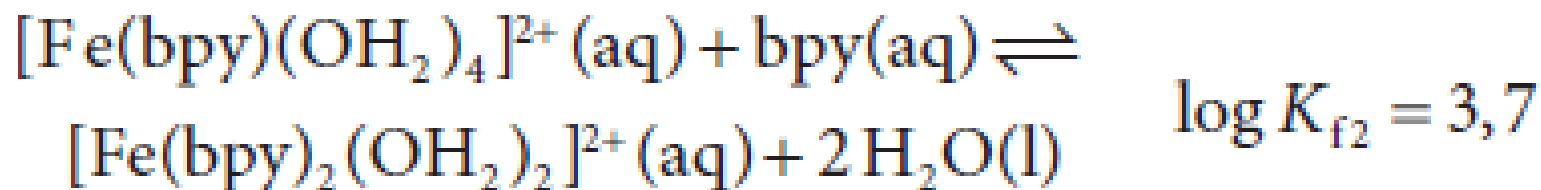
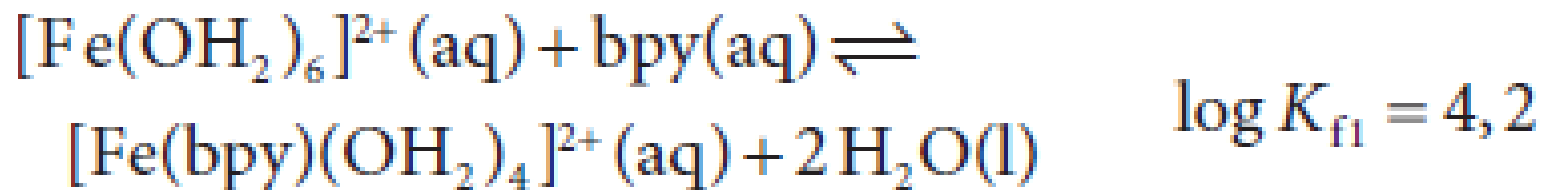
(b)

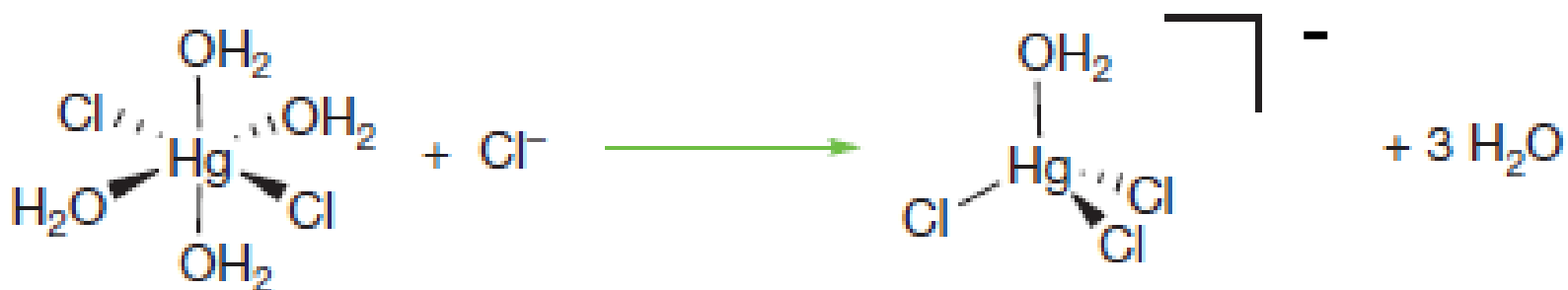
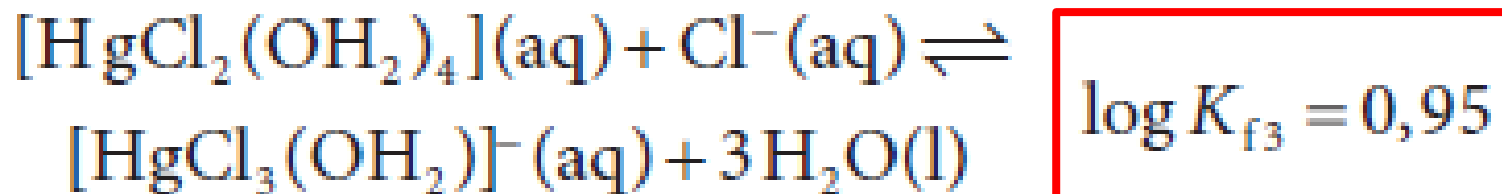
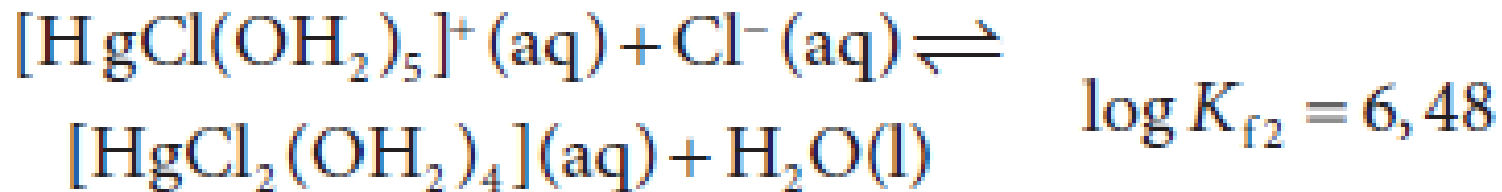
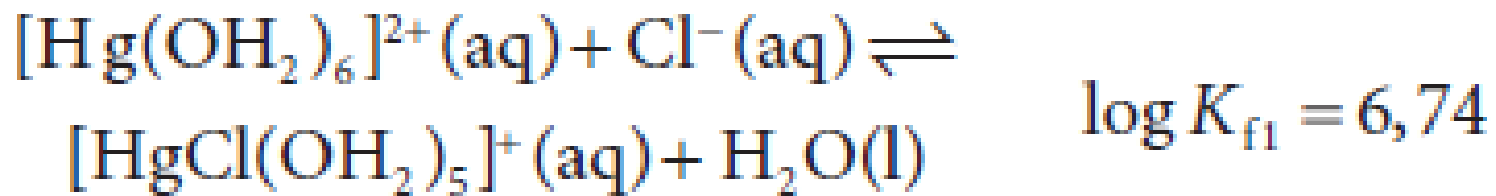


(c)

Anelli chelati a 6 termini

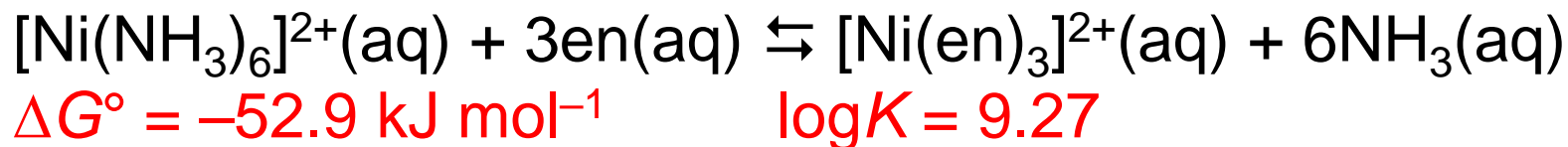
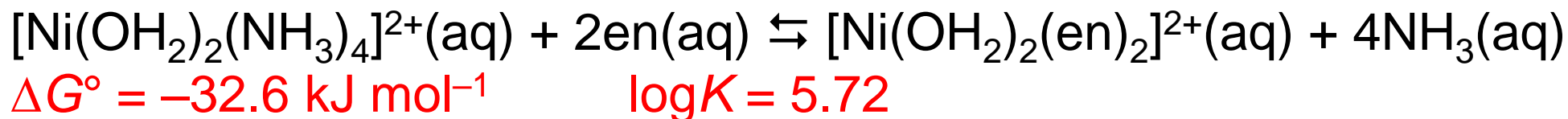
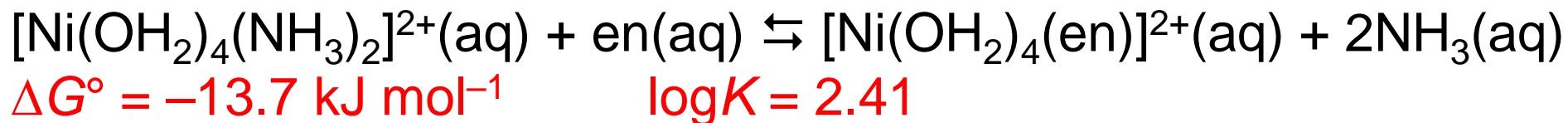
Un'inversione nell'andamento  $Kf_n > Kf_{n+1}$  è normalmente un'indicazione di una grande variazione nella struttura elettronica del complesso



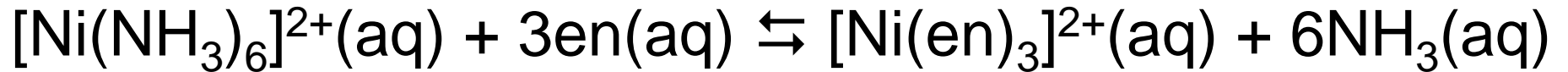




# Effetto chelante



# Effetto chelante



$$\log K = 9.27$$

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

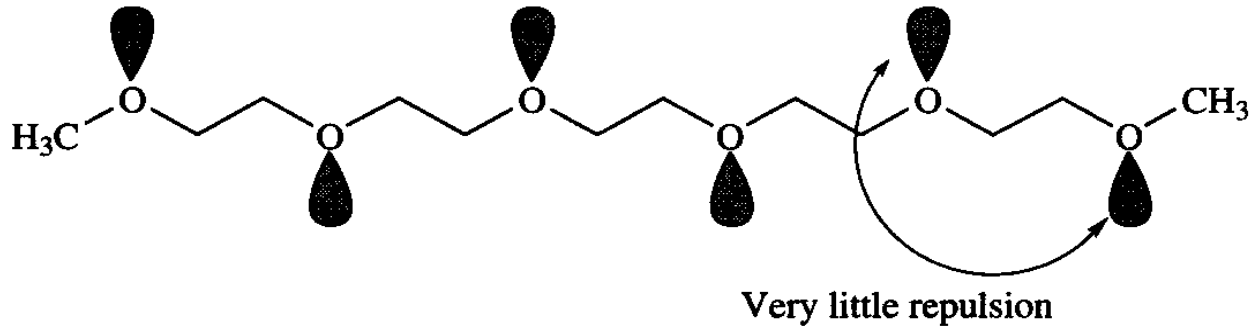
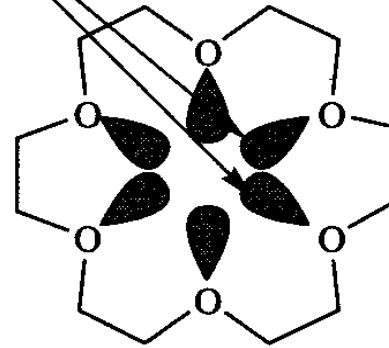
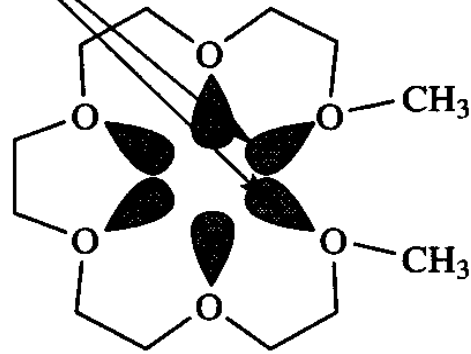
$$\Delta H^\circ = -16.8 \text{ kJ mol}^{-1}$$

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

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

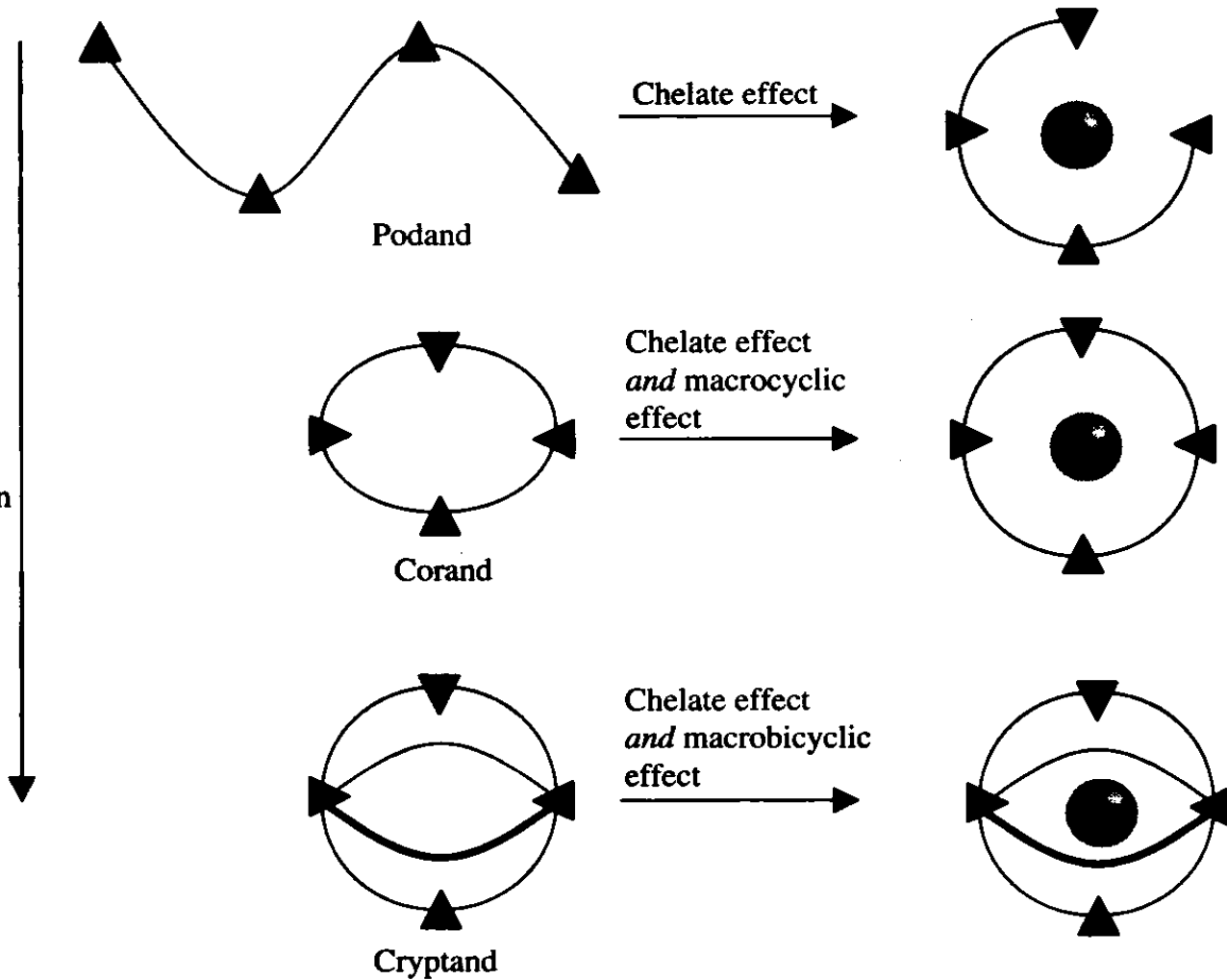
# Effetto macrociclo

Lone pair–lone pair repulsive interaction



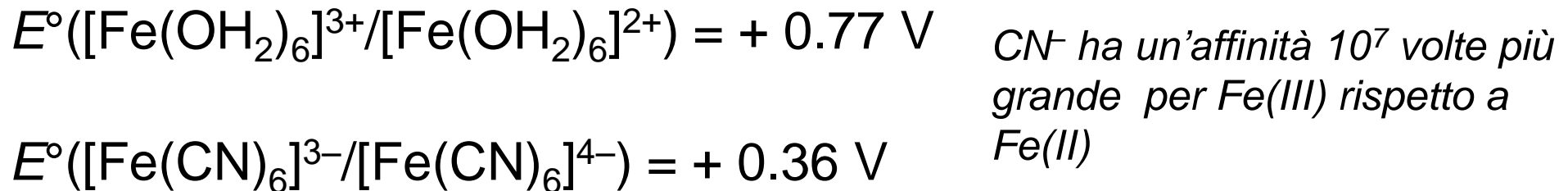
podando

Increasing  
degree  
of host  
organisation



# Influenza della complessazione sul potenziale standard di uno ione metallico M

*la capacità di un complesso ML di accettare o cedere un elettrone è diversa da quella del corrispondente aquoione M*



*La variazione di potenziale standard per la coppia redox di ML rispetto a quello di M riflette la tendenza di L a coordinarsi più fortemente alla forma ossidata o a quella ridotta di M*

- La formazione di un complesso termodinamicamente più stabile quando il metallo è nello stato di ossidazione più alto di una coppia redox favorisce la sua ossidazione e rende il potenziale standard più negativo.*
- La formazione di un complesso più stabile quando il metallo è nello stato di ossidazione più basso di una coppia redox favorisce la sua riduzione e il potenziale standard diventa più positivo,*

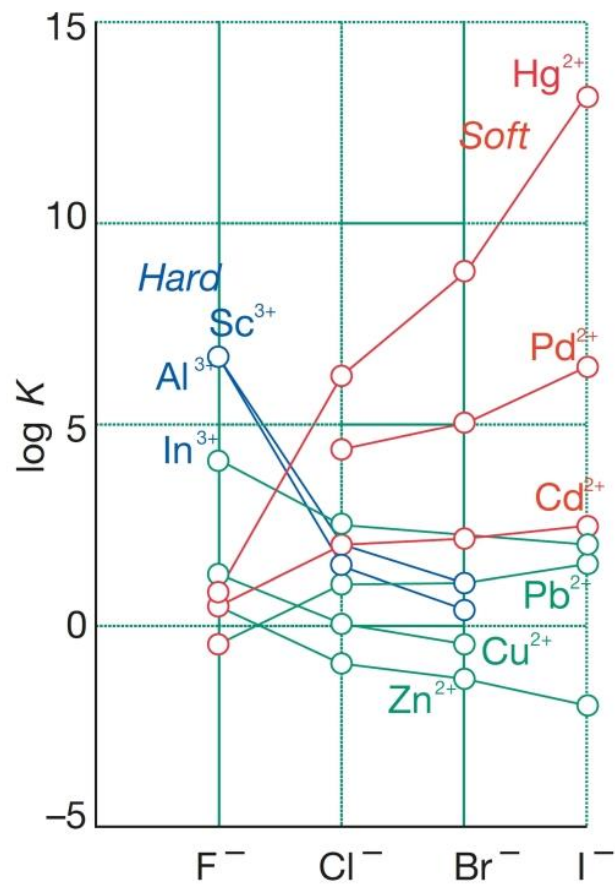
# Influenza della complessazione sul potenziale standard di uno ione metallico M

$$E^\circ([\text{Ru}(\text{OH}_2)_6]^{3+}/[\text{Ru}(\text{OH}_2)_6]^{2+}) = + 0.25 \text{ V}$$

$$E^\circ([\text{Ru}(\text{CN})_6]^{3-}/[\text{Ru}(\text{CN})_6]^{4-}) = + 0.80 \text{ V}$$

# Costanti di formazione di ioni metallici con alogenuri

Metal ion	log $K_1$			
	X = F	X = Cl	X = Br	X = I
<b>a</b> $\text{Fe}^{3+}(\text{aq})$	6.0	1.4	0.5	–
<b>b</b> $\text{Hg}^{2+}(\text{aq})$	1.0	6.7	8.9	12.9



# Hard and Soft Acids and Bases (HSAB) Principle (Pearson)

$F > O > N > Cl > Br > C \approx I \approx S > Se > P > As > Sb$

*elettronegatività*



*Hard*

*Soft*

$F > Cl > Br > I$

$O \gg S > Se > Te$

$N \gg P > As > Sb$

$F < Cl < Br < I$

$O \ll S > Se \approx Te$

$N \ll P > As > Sb$



# HSAB principle

## Metal centres (Lewis acids)

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

---

# 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), $ArNH_2$ , $[NO_2]^-$ , $[SO_3]^{2-}$

---

# HSAB principle

**gli acidi *hard* formano complessi più stabili con basi *hard* e gli acidi *soft* formano complessi più stabili con basi *soft***