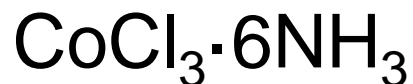


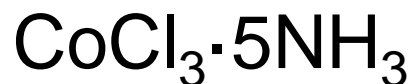
Chimica di coordinazione



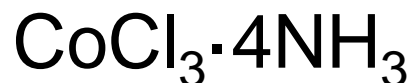
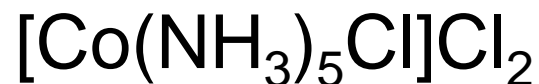
Alfred Werner 1866 – 1919
Premio Nobel per la chimica 1913



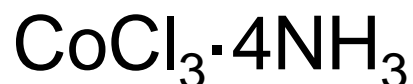
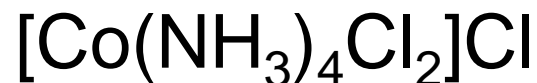
Giallo



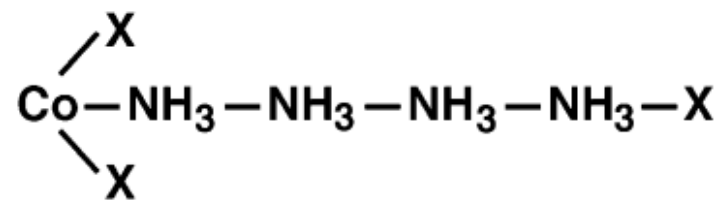
Rosso-viola



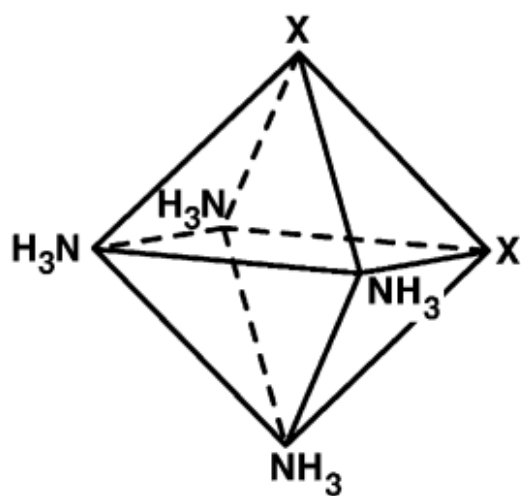
Verde



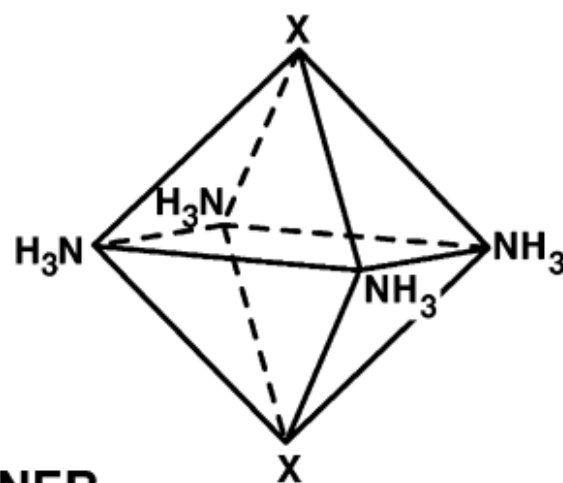
Violetto



JØRGENSEN



WERNER

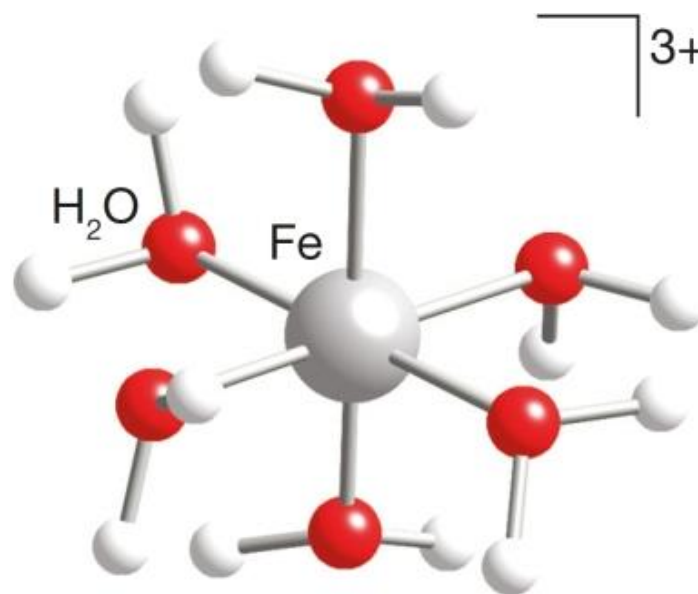
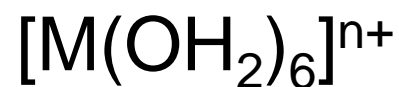
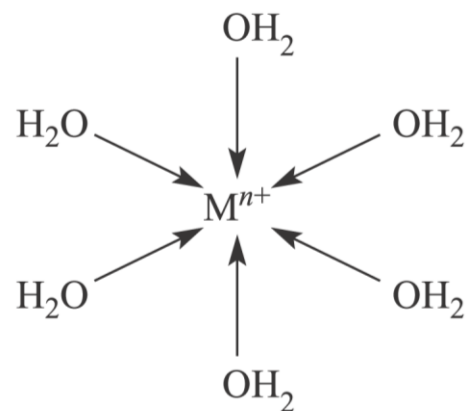
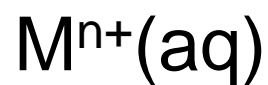
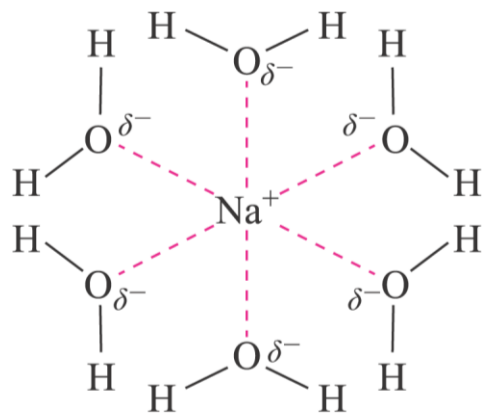


Composti di coordinazione

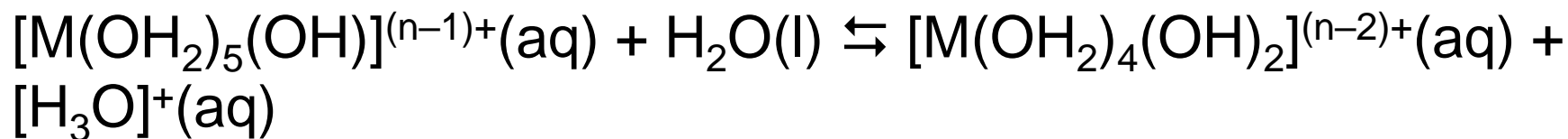
(Werner's type complexes)

- In un composto di coordinazione (o complesso) un atomo (o ione) centrale è coordinato da molecole o ioni (solitamente tra 2 e 9), i **leganti**, 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**.
- La chimica dei composti di coordinazione *tipo Werner* è prevalentemente in soluzione acquosa.

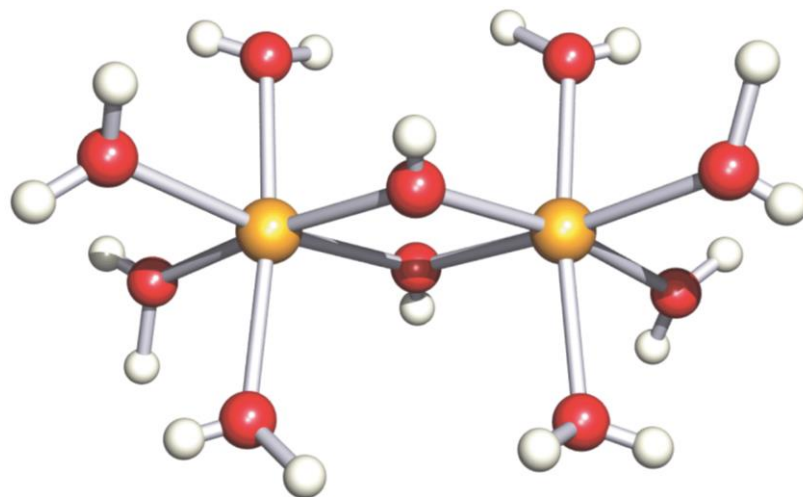
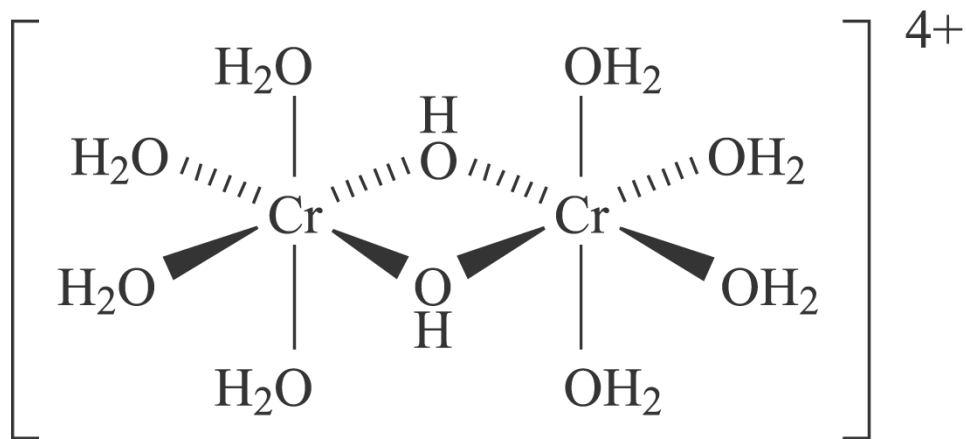
Interazione elettrostatica o parzialmente covalente



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

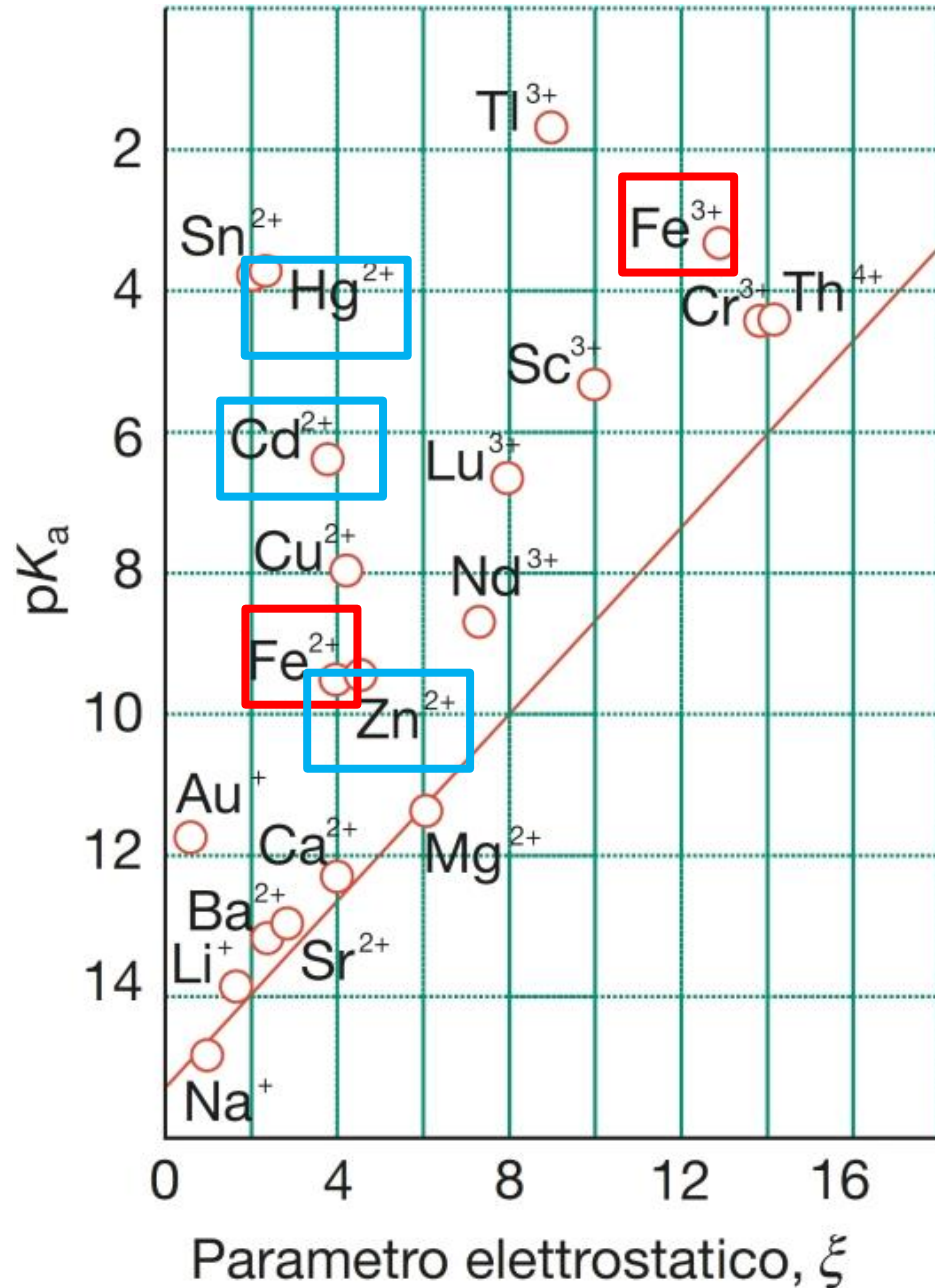
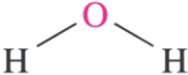
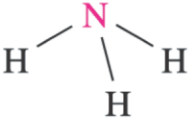

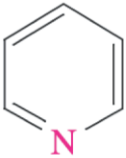

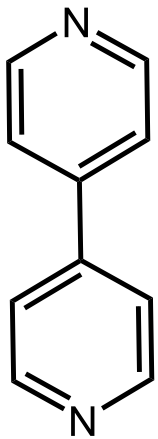


FIGURA 5.4 La correlazione fra la costante di acidità pK_a e il parametro elettrostatico adimensionale ξ ($= 100z^2/(r/pm)$) per aquoioni. La retta indica l'andamento atteso in base al modello ionico.

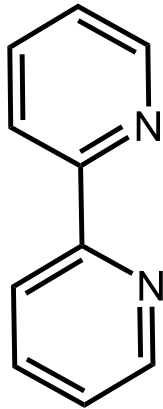
Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
Water		Monodentate	
Ammonia		Monodentate	
Tetrahydrofuran	THF	Monodentate	
Pyridine	py	Monodentate	
1,2-Ethanediamine [†]	en	Bidentate	

[†] 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.

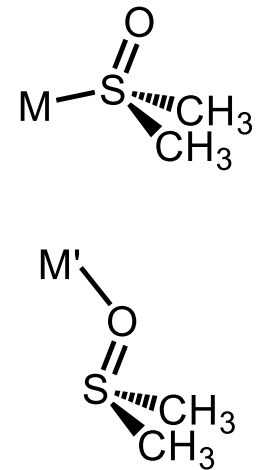
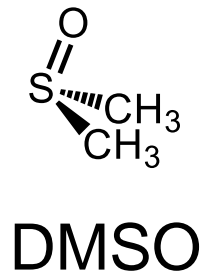
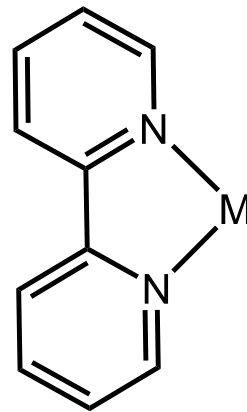
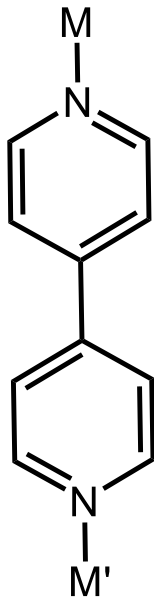
- Leganti politopici
- Leganti polidentati (chelanti)
- Leganti ambidentati



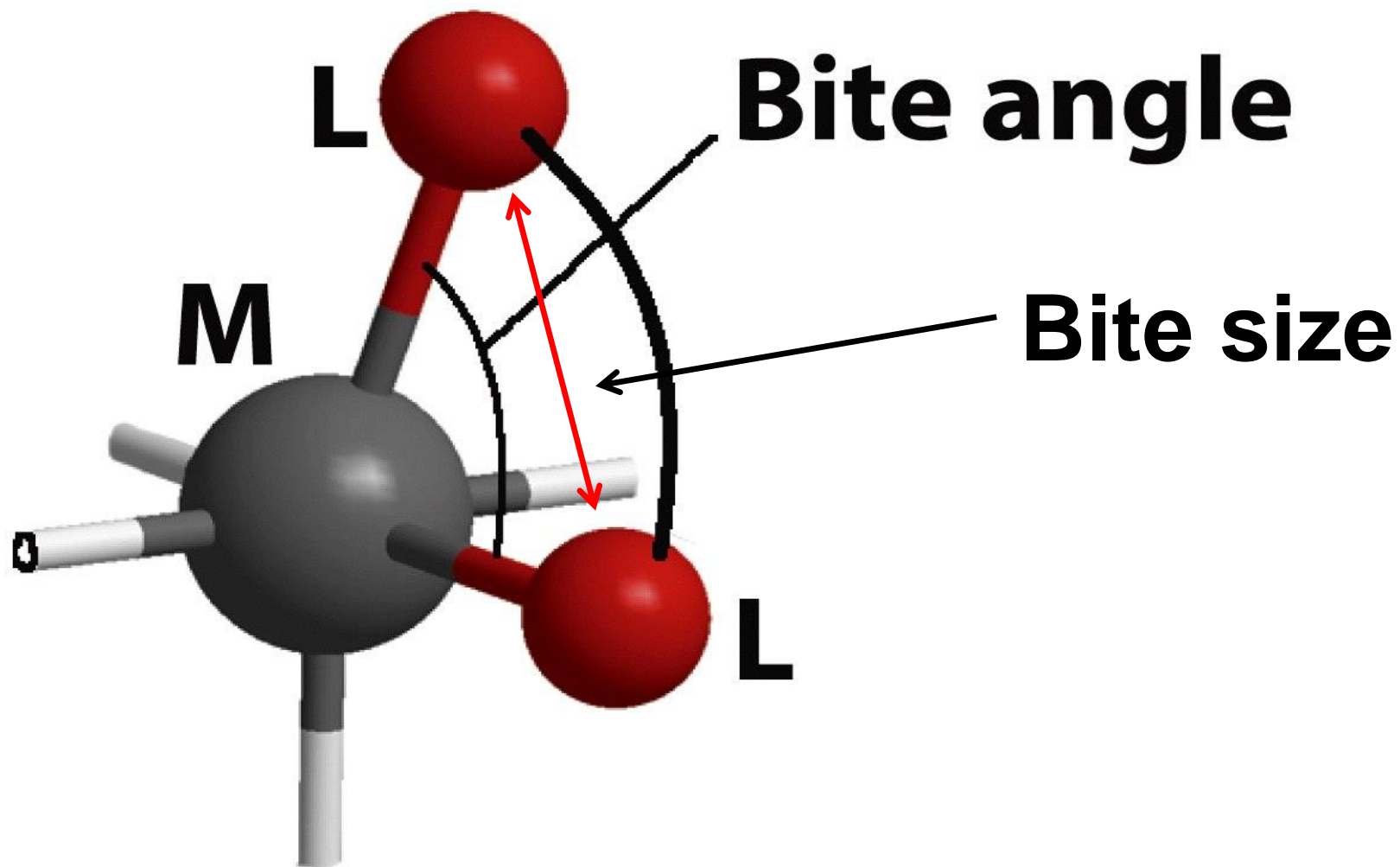
4,4'-bpy

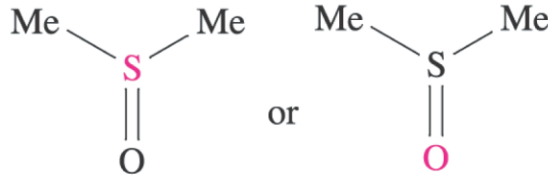
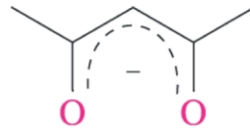
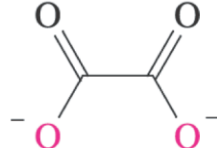
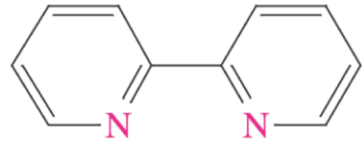


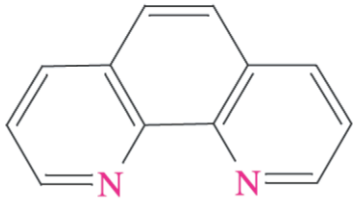


2,2'-bpy



Chelanti

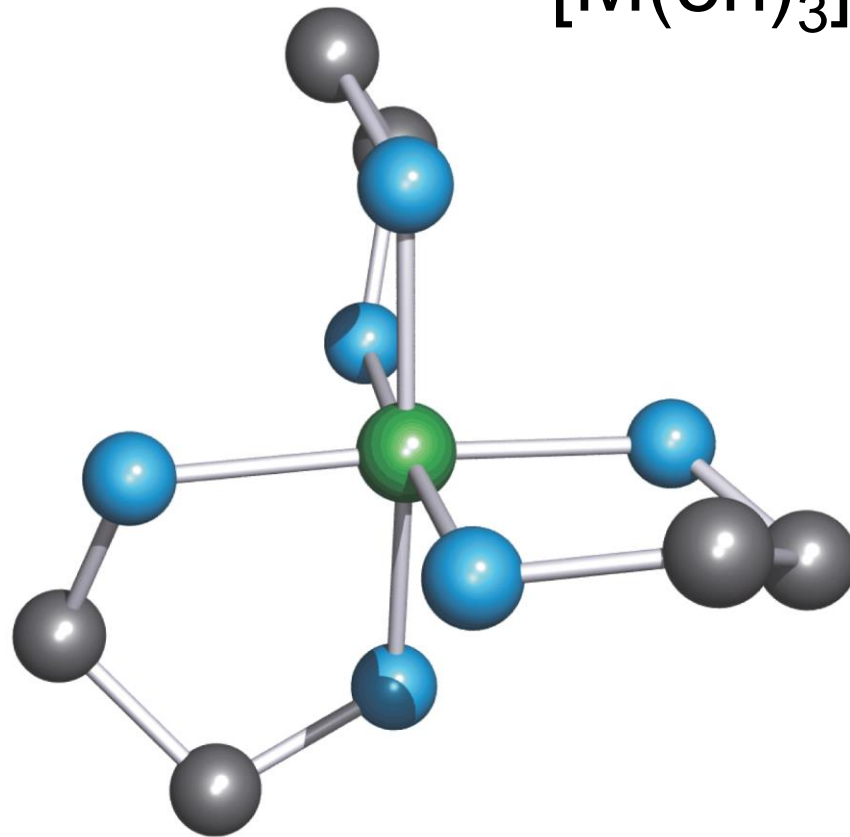


Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
Dimethylsulfoxide	DMSO	Monodentate	
Acetylacetonate ion	[acac] ⁻	Bidentate	
Oxalate or ethanedioate ion	[ox] ²⁻	Bidentate	
2,2'-Bipyridine	bpy or bipy	Bidentate	

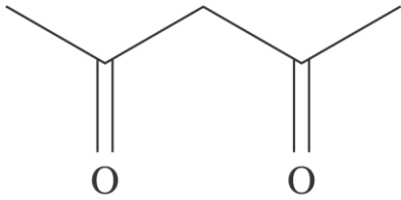
Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
1,10-Phenanthroline	phen	Bidentate	
1,4,7-Triazaheptane [†]	dien	Tridentate	
1,4,7,10-Tetraazadecane [†]	trien	Tetradentate	
<i>N,N,N',N'</i> -Ethylenediaminetetraacetate ion [‡]	[EDTA] ⁴⁻	Hexadentate	See equation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

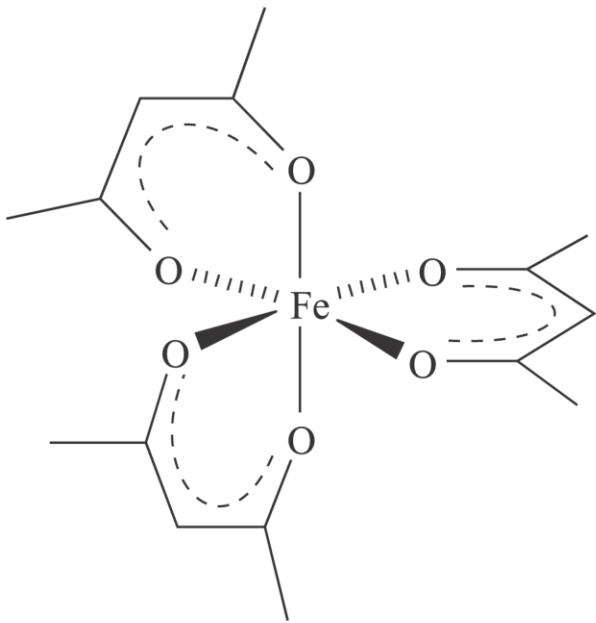
[‡] Although not systematic by the IUPAC rules, this is the commonly accepted name for this anion.



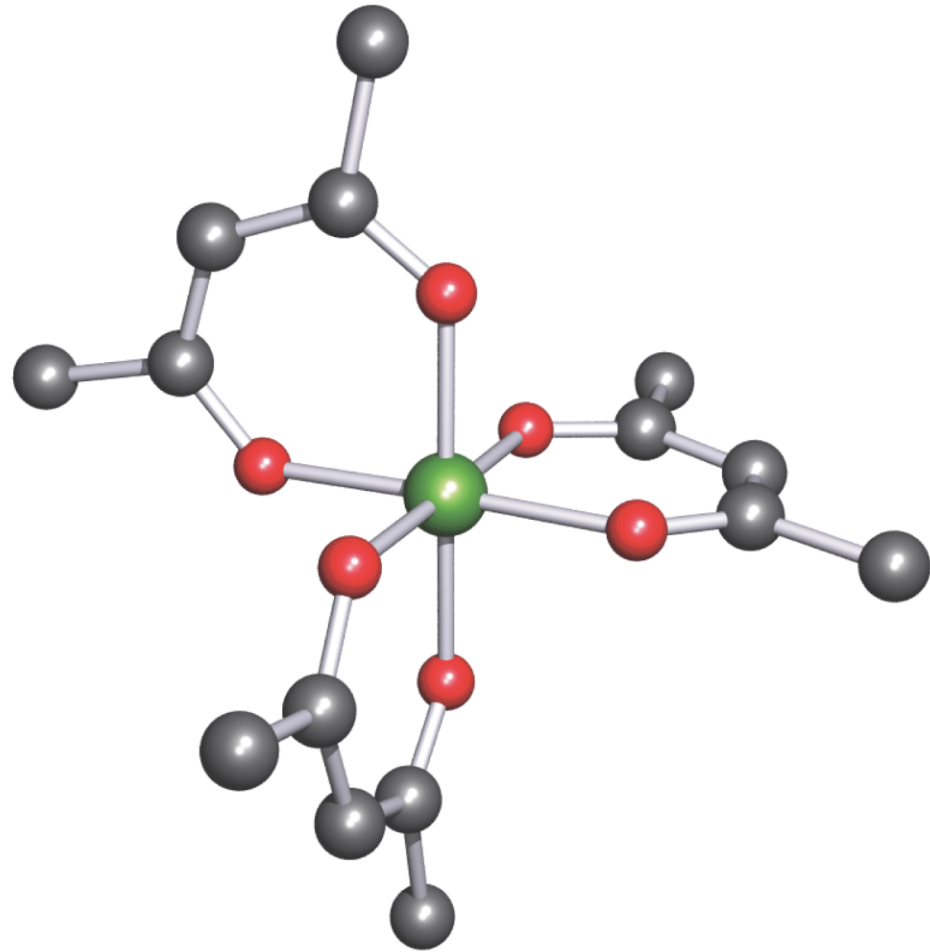
Anelli chelati a 5 termini



(a)



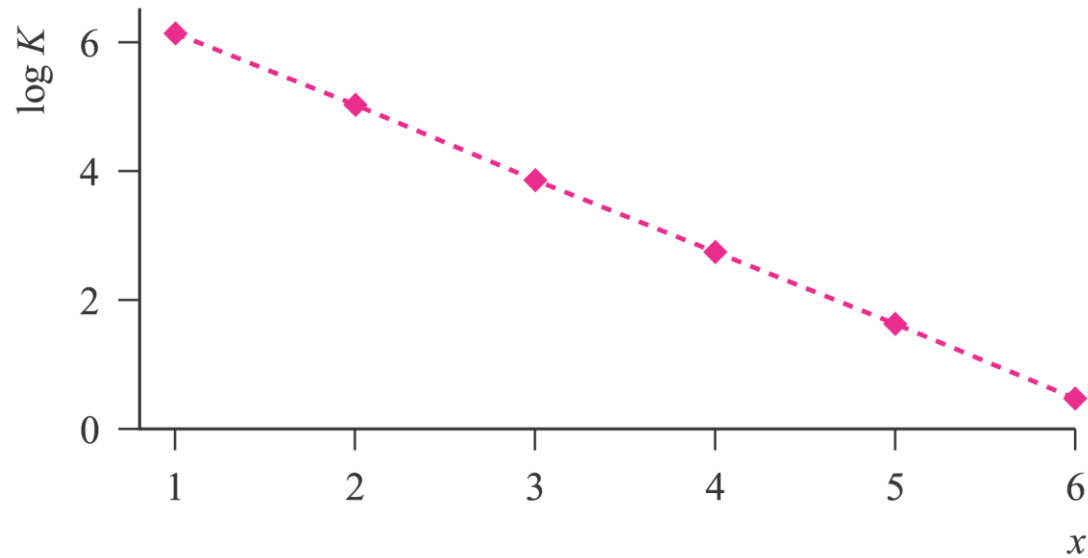
(b)



(c)

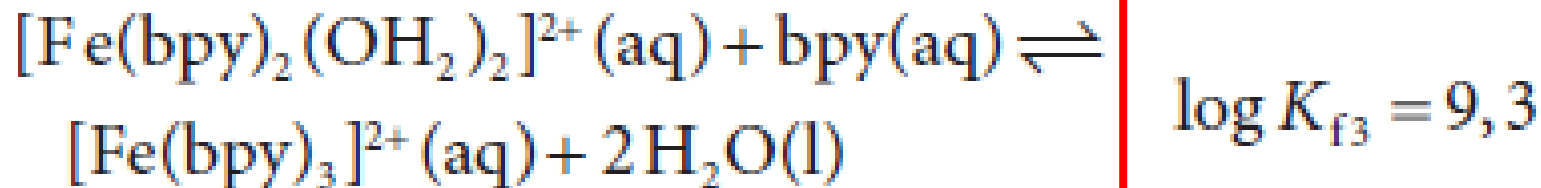
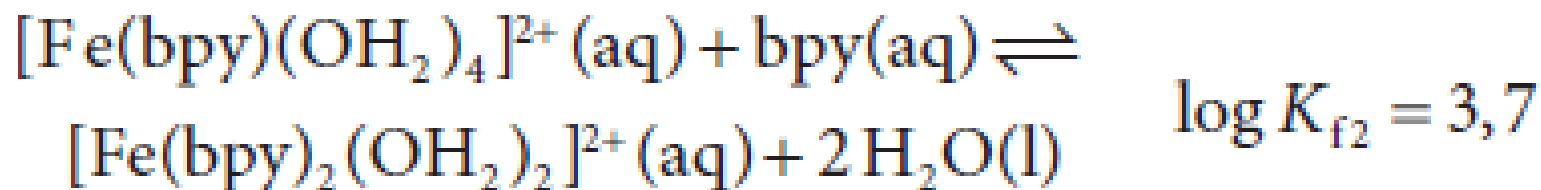
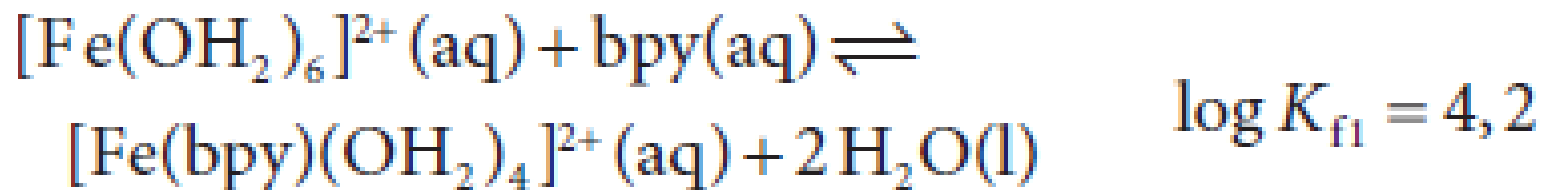
Anelli chelati a 6 termini

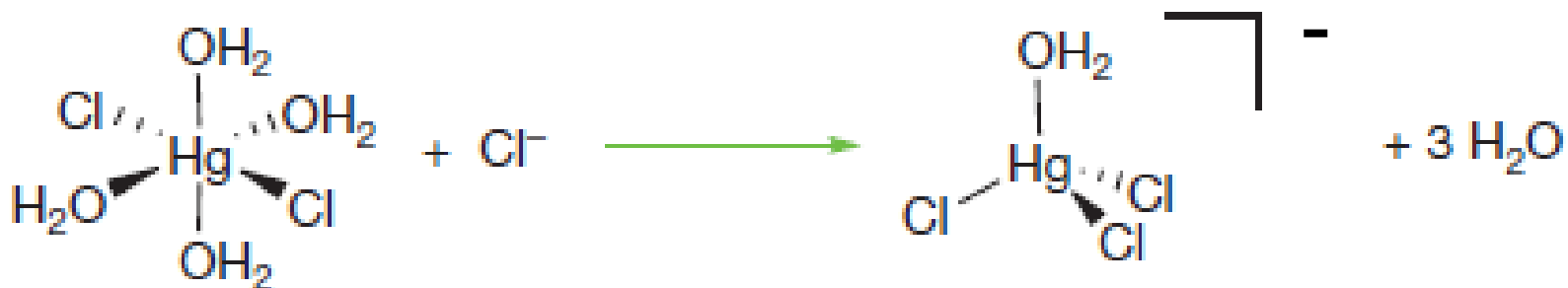
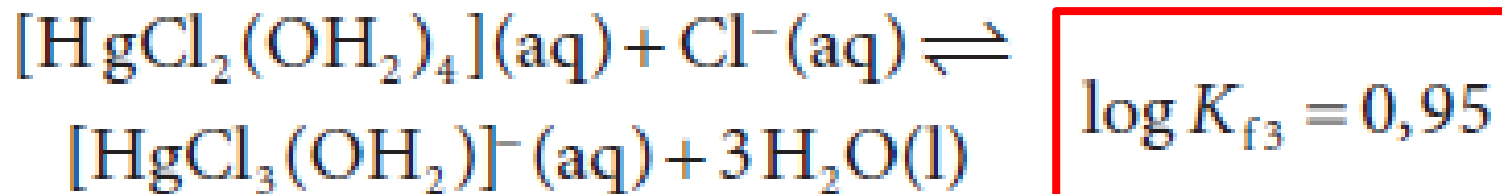
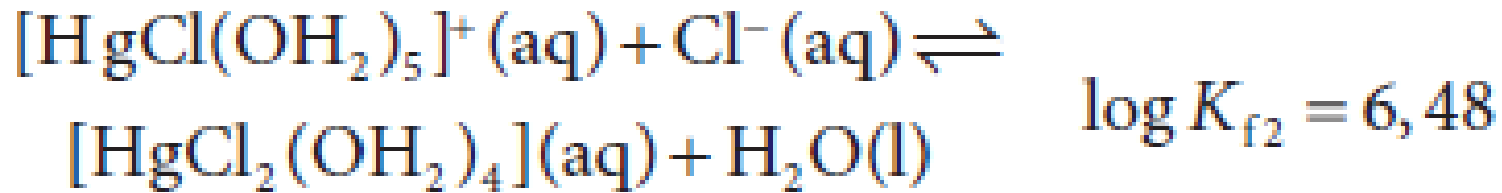
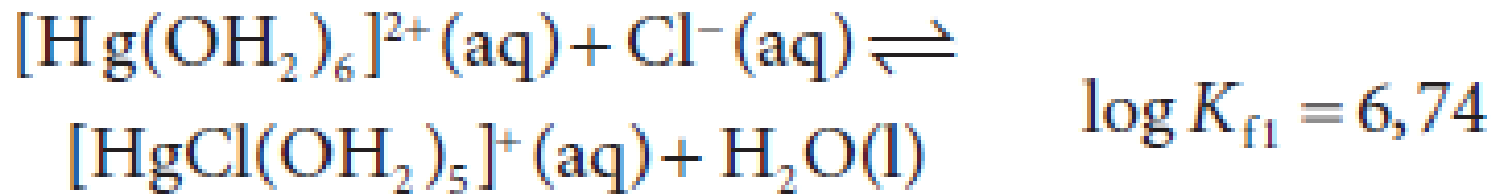
Costanti di stabilità parziali per la formazione di $[M(OH_2)_{6-x}L_x]^{n+}$



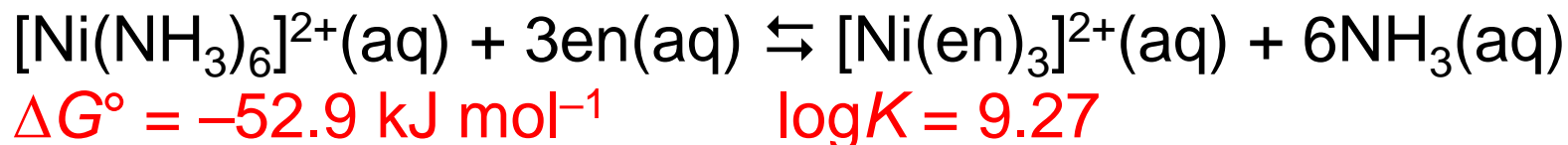
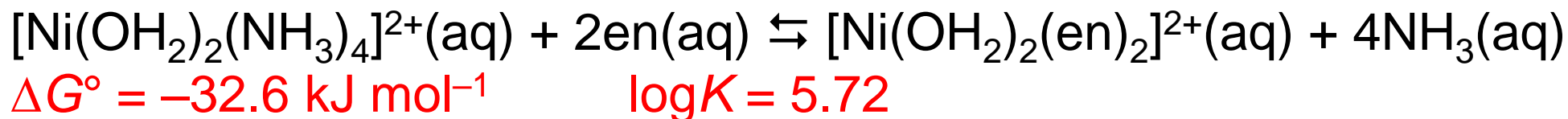
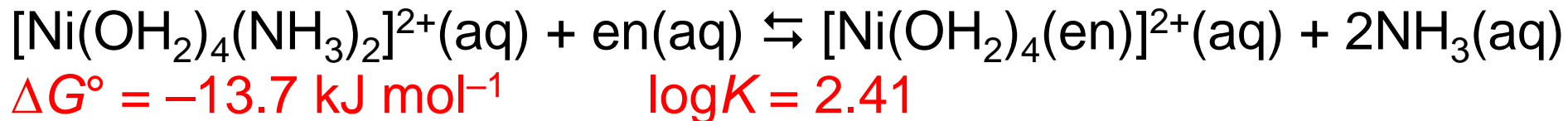
$$\beta = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6$$

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

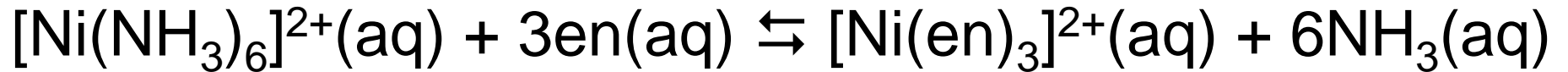




Effetto chelante



Effetto chelante



$$\log K = 9.27$$

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

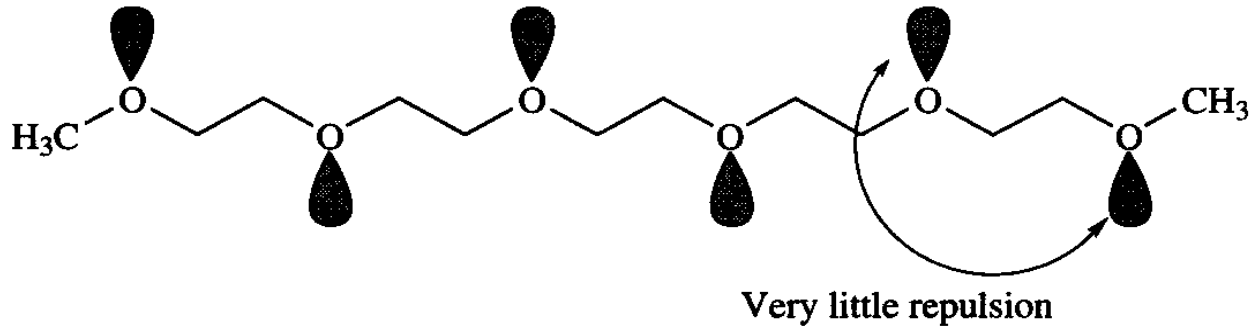
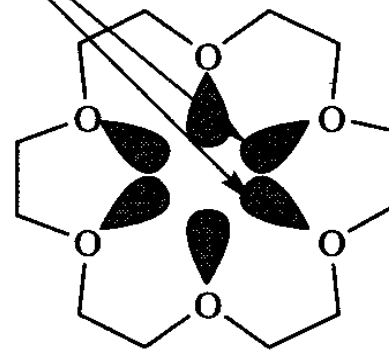
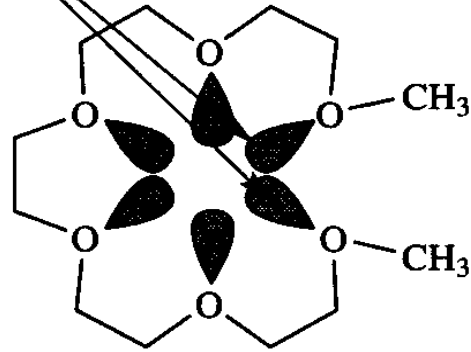
$$\Delta H^\circ = -16.8 \text{ kJ mol}^{-1}$$

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

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

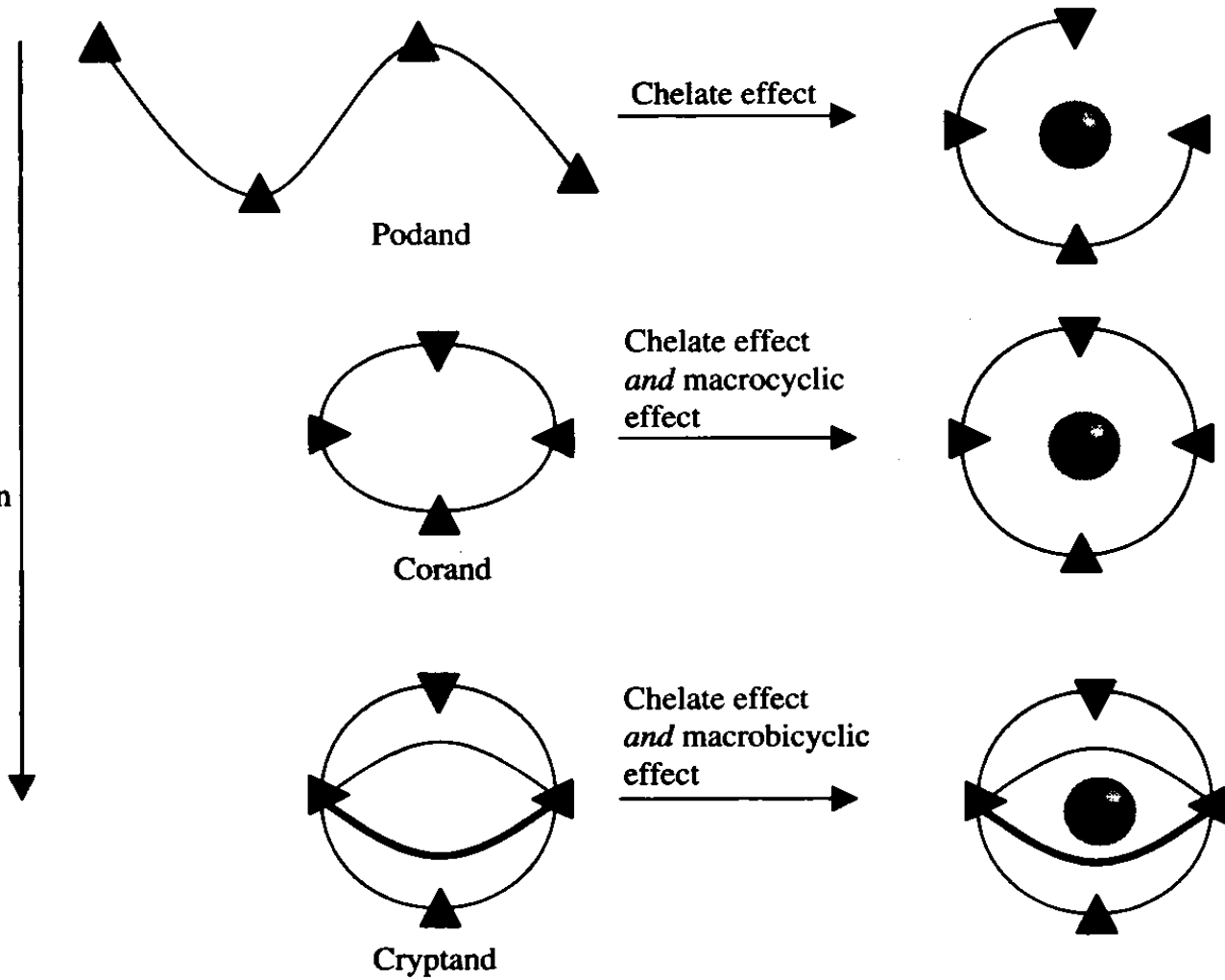
Effetto macrociclo

Lone pair-lone pair repulsive interaction



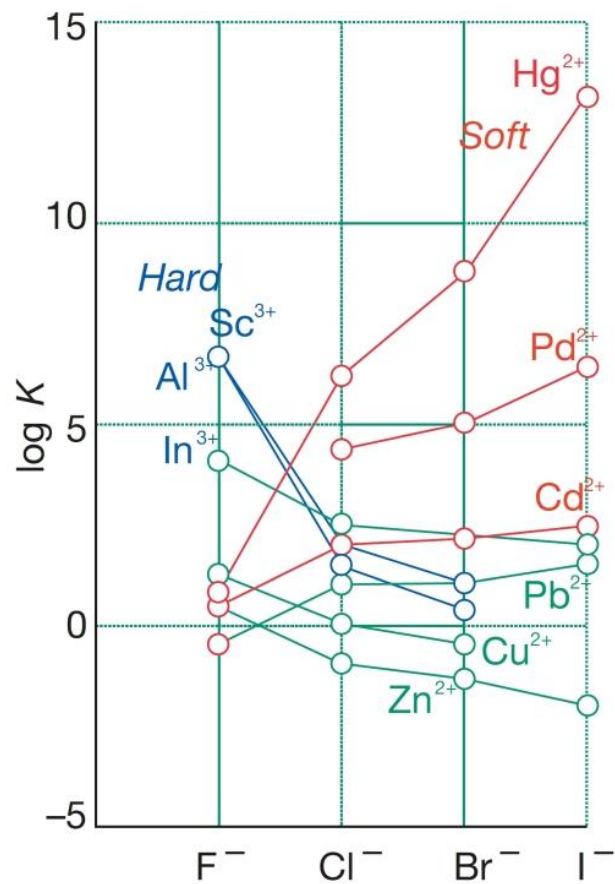
podando

Increasing
degree
of host
organisation



Costanti di formazione di ioni metallici con alogenuri

Metal ion	log K_1			
	X = F	X = Cl	X = Br	X = I
a $\text{Fe}^{3+}(\text{aq})$	6.0	1.4	0.5	–
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



Acidi Hard

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

HSAB Principle

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

Influenza della complessazione sul potenziale standard di uno ione metallico M

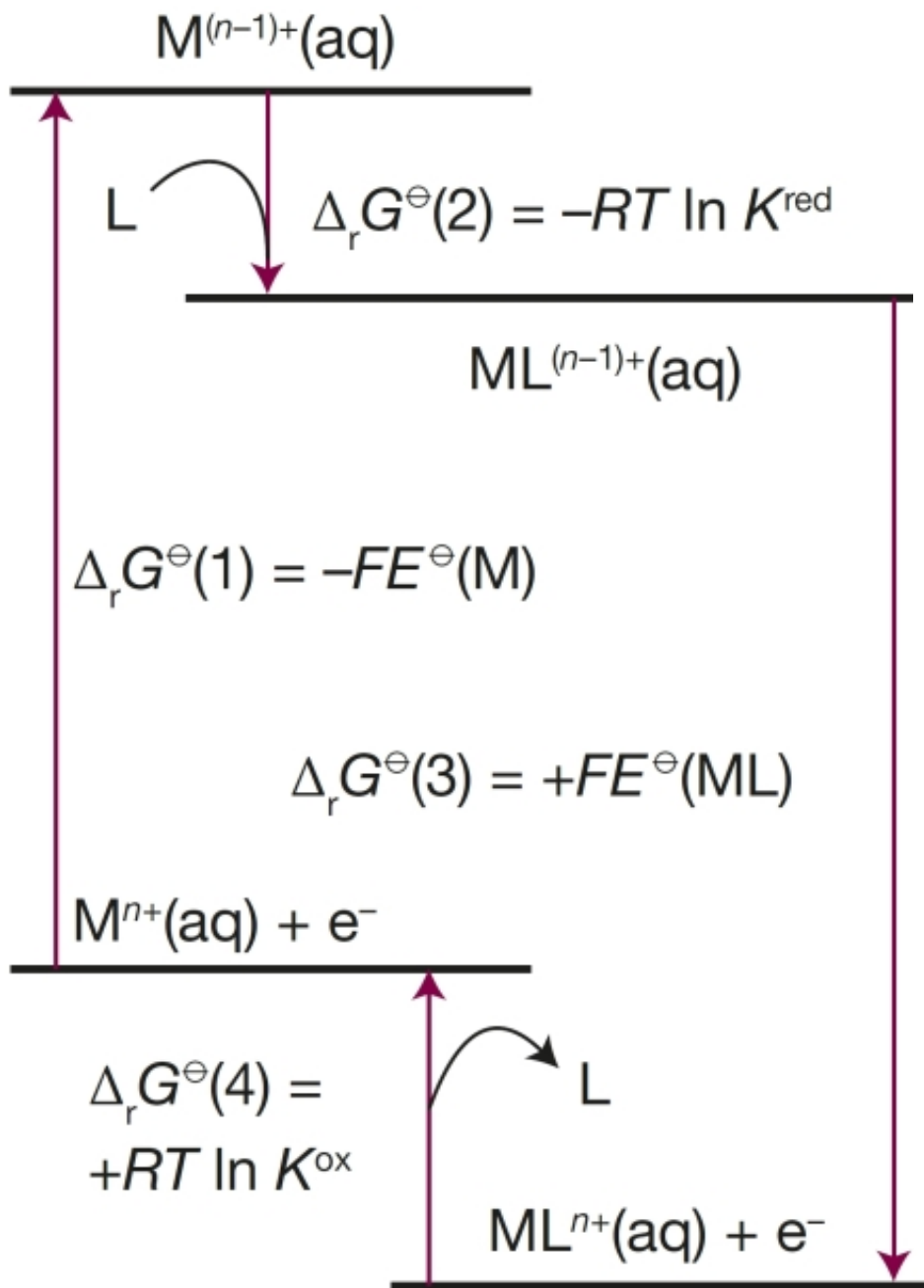
la capacità di un complesso ML di accettare o cedere un elettrone è diversa da quella del corrispondente aquoione M

$$E^\circ([\text{Fe}(\text{OH}_2)_6]^{3+}/[\text{Fe}(\text{OH}_2)_6]^{2+}) = + 0.77 \text{ V}$$

$$E^\circ([\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}) = + 0.36 \text{ V}$$

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,*



$$E^\ominus(M) - E^\ominus(ML) = (0,059 \text{ V}) \log \frac{K^{\text{ox}}}{K^{\text{red}}}$$

ogni volta che la costante di equilibrio per la coordinazione del legante a M^{v+} (K_{ox}) aumenta di dieci volte rispetto a quella per la coordinazione a $M^{(v-1)+}$ (K_{red}), il potenziale di riduzione diminuisce di 0,059 V.

Influenza della complessazione sul potenziale standard di uno ione metallico M

$$E^\circ([\text{Fe}(\text{OH}_2)_6]^{3+}/[\text{Fe}(\text{OH}_2)_6]^{2+}) = + 0.77 \text{ V}$$

$$E^\circ([\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}) = + 0.36 \text{ V}$$

CN⁻ ha un'affinità 10⁷ volte più grande per Fe(III) rispetto a Fe(II)

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

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