

Chimica di coordinazione



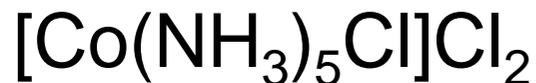
Alfred Werner 1866 – 1919
Premio Nobel per la chimica 1913



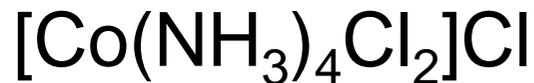
Giallo



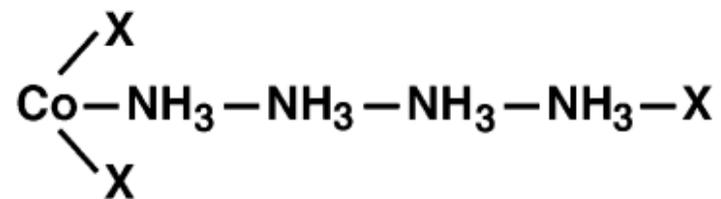
Rosso-viola



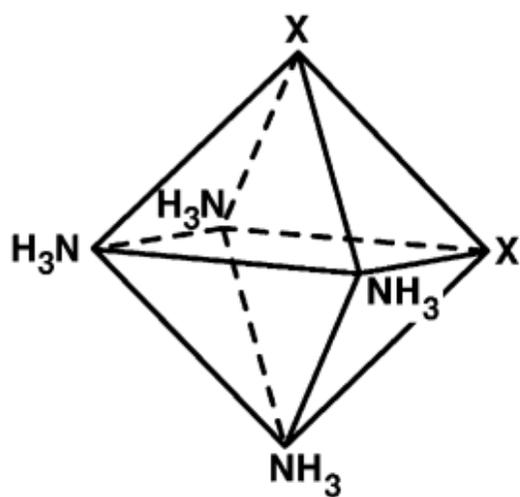
Verde



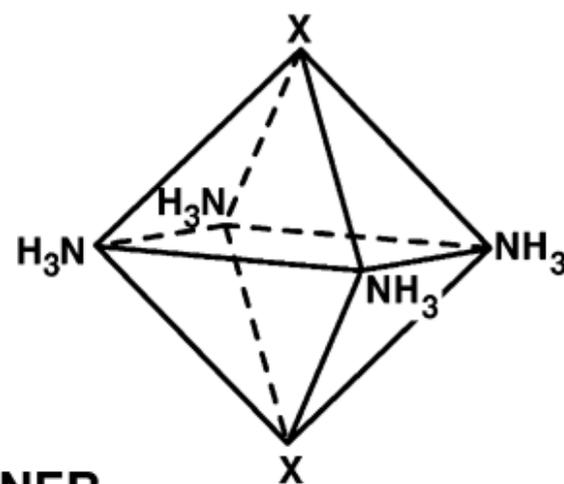
Violetto



JØRGENSEN



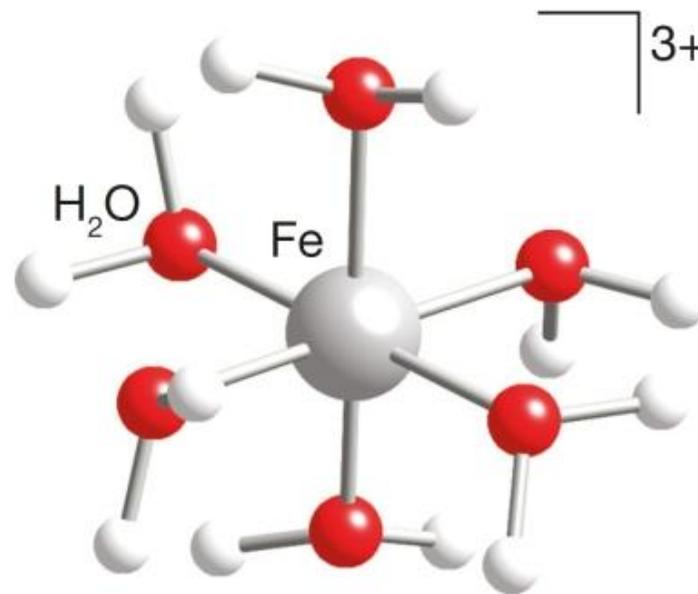
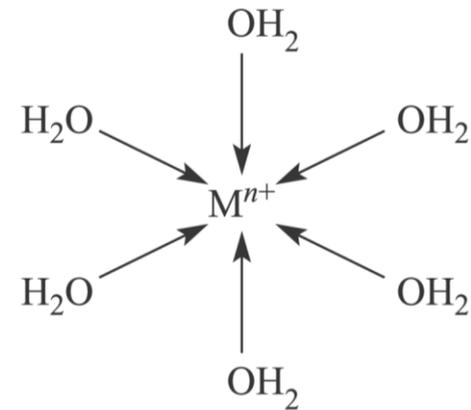
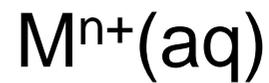
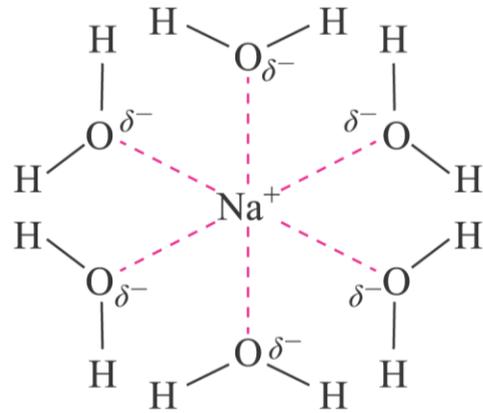
WERNER



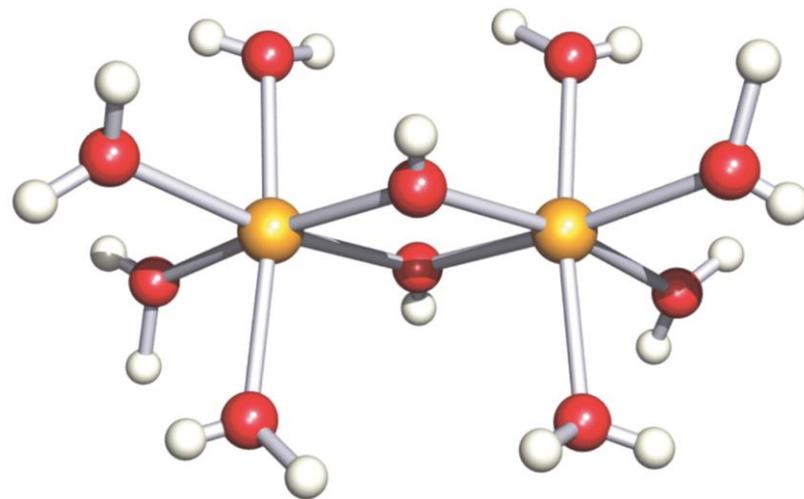
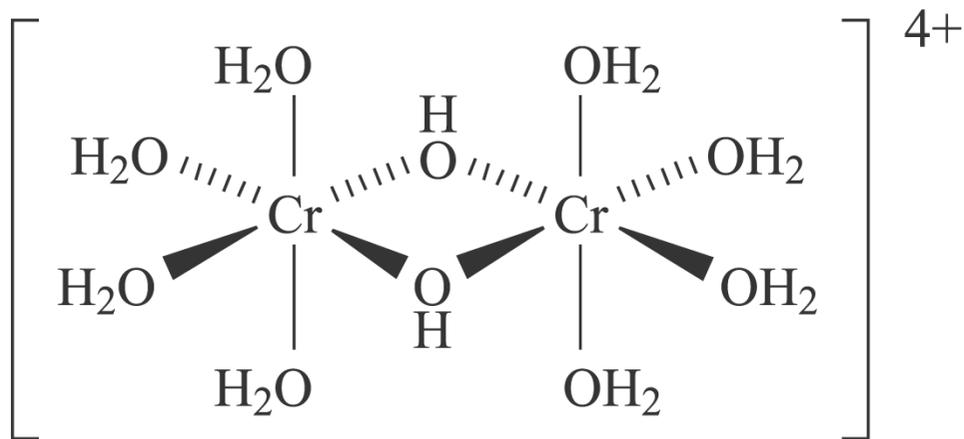
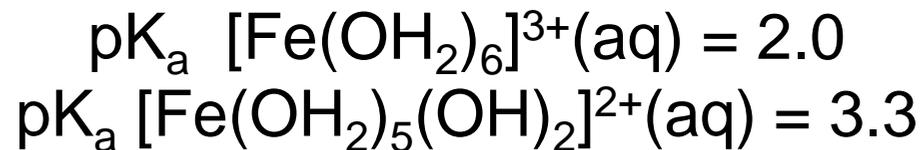
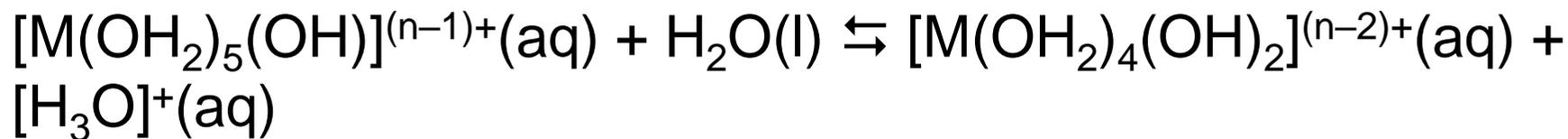
Composti di coordinazione

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



Forza degli aquoacidi

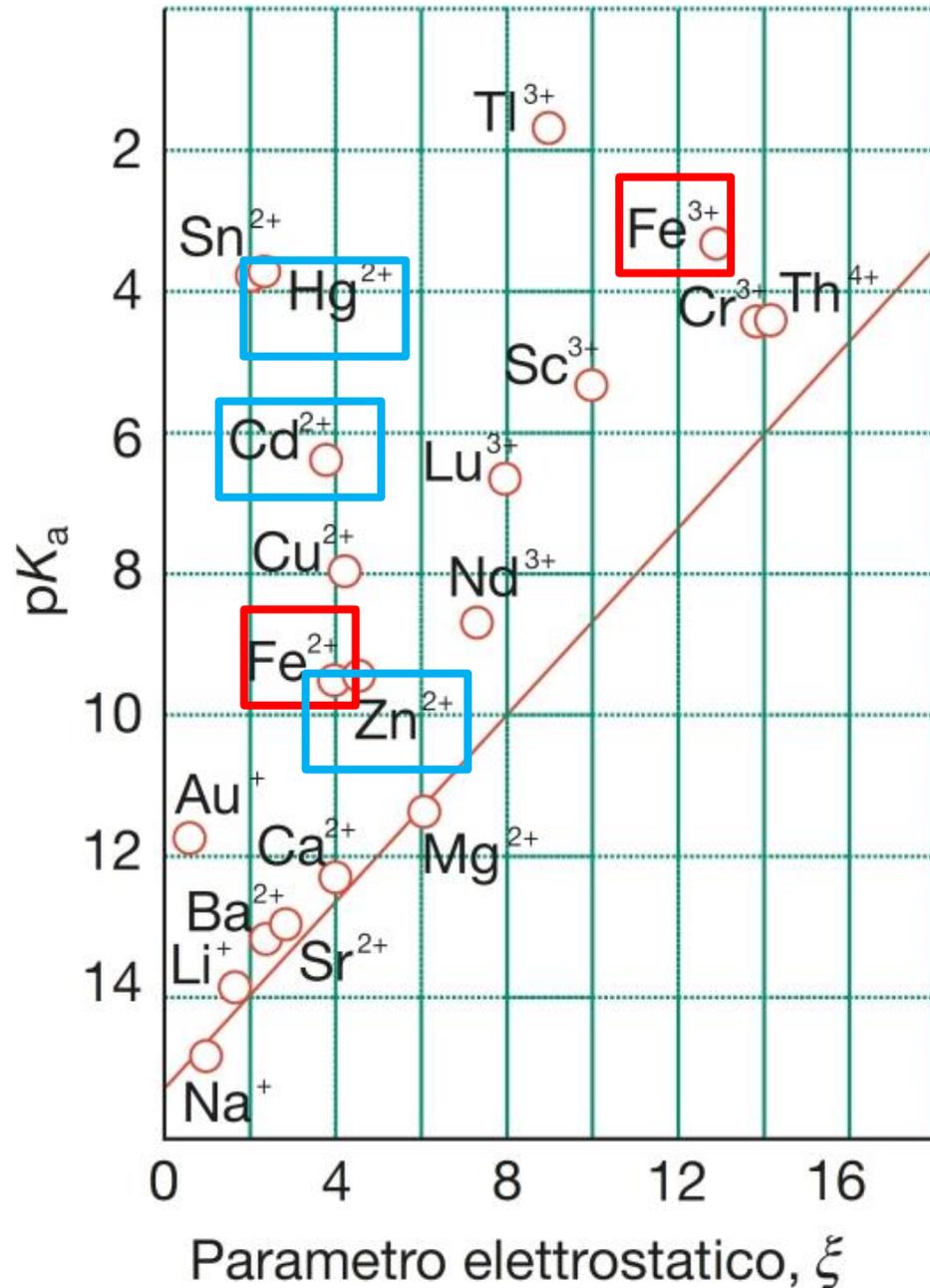
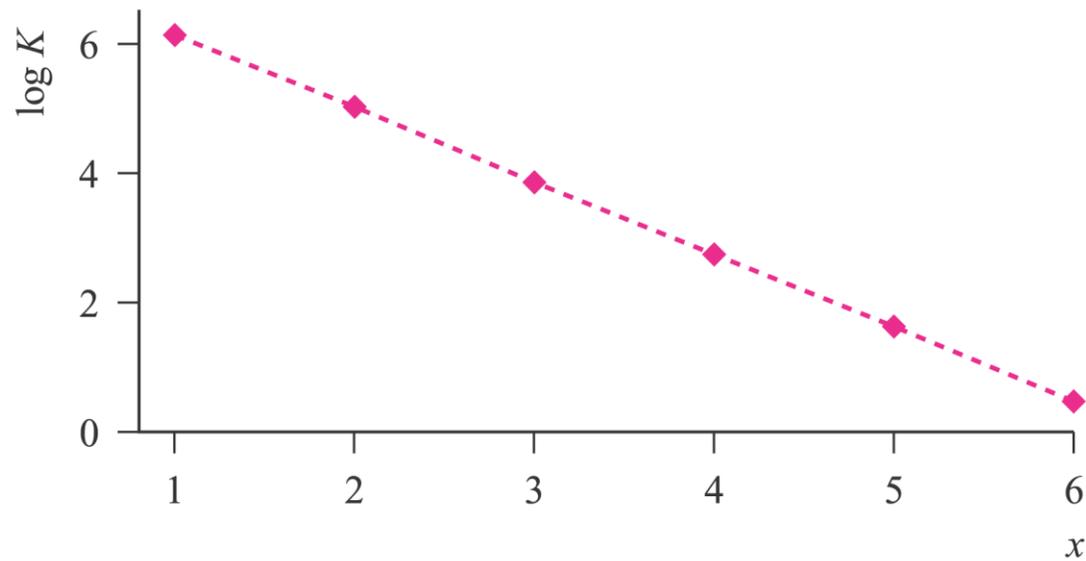


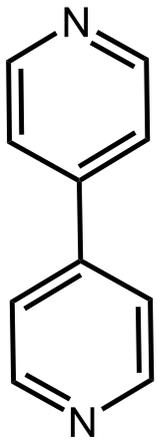
FIGURA 5.4 La correlazione fra la costante di acidità pK_a e il parametro elettrostatico adimensionale ξ ($= 100z^2/(r/pm)$) per aquoioni. La retta indica l'andamento atteso in base al modello ionico.

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

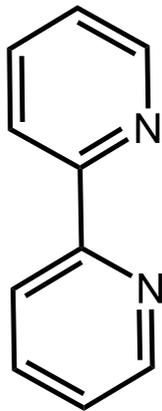


$$\beta = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6$$

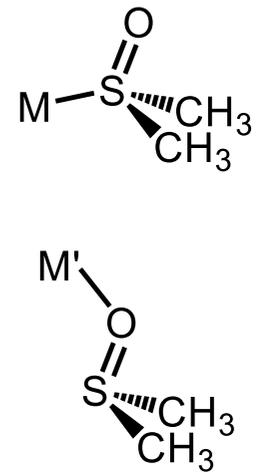
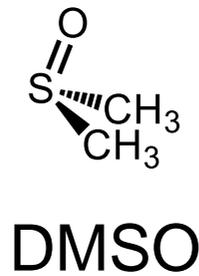
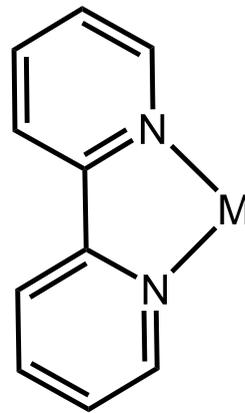
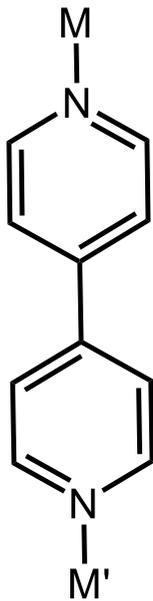
- Leganti politopici
- Leganti polidentati (chelanti)
- Leganti ambidentati



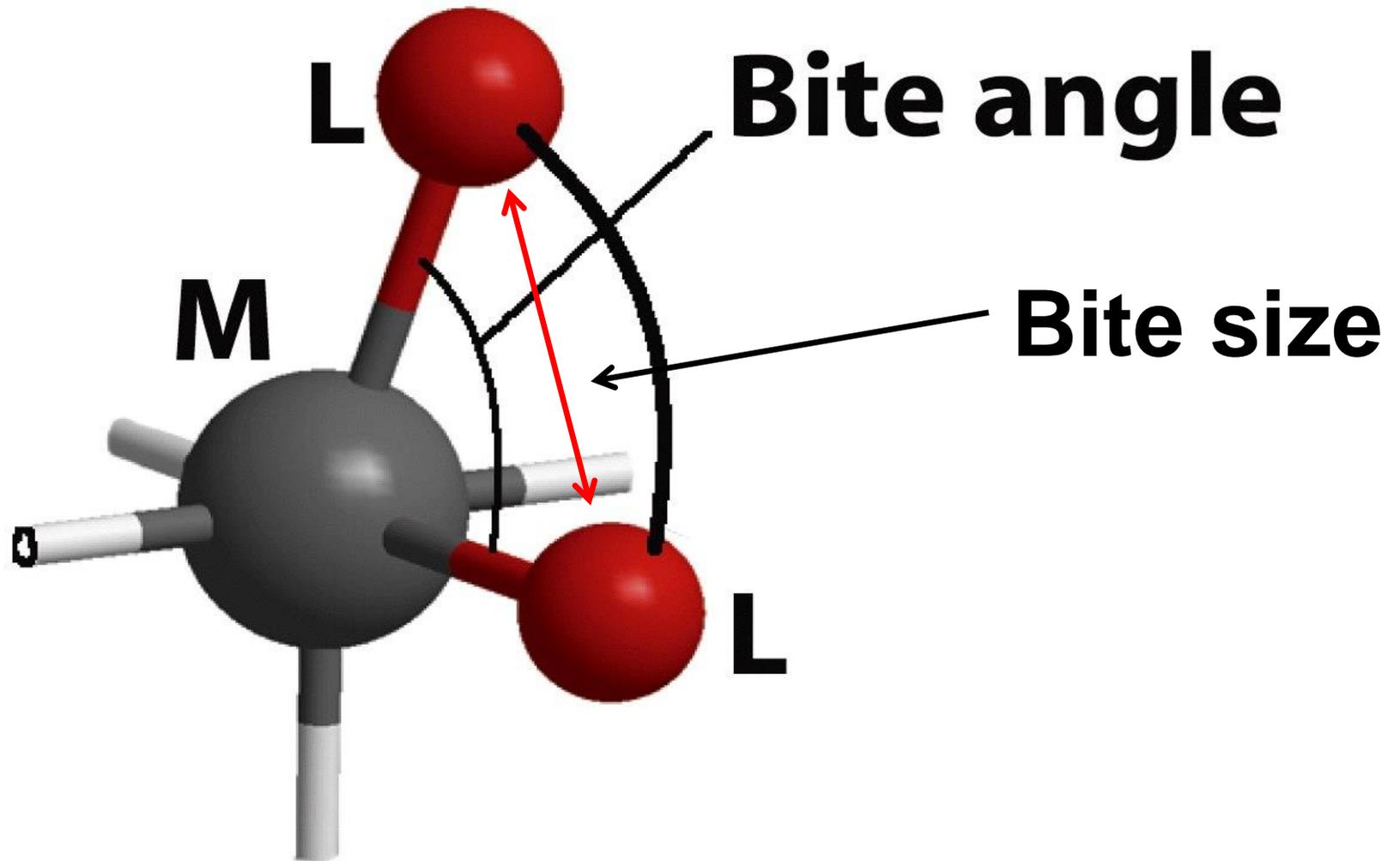
4,4'-bpy

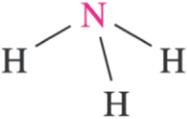


2,2'-bpy

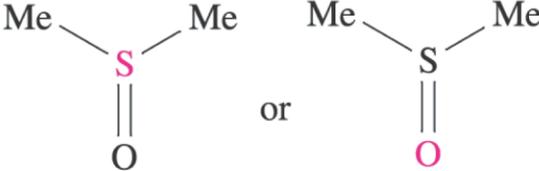
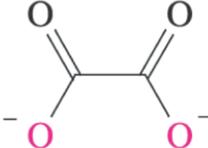


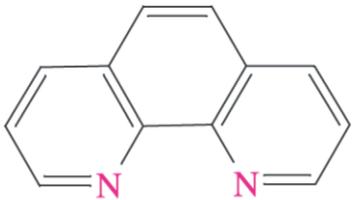
Chelanti



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 [†]	en	Bidentate	

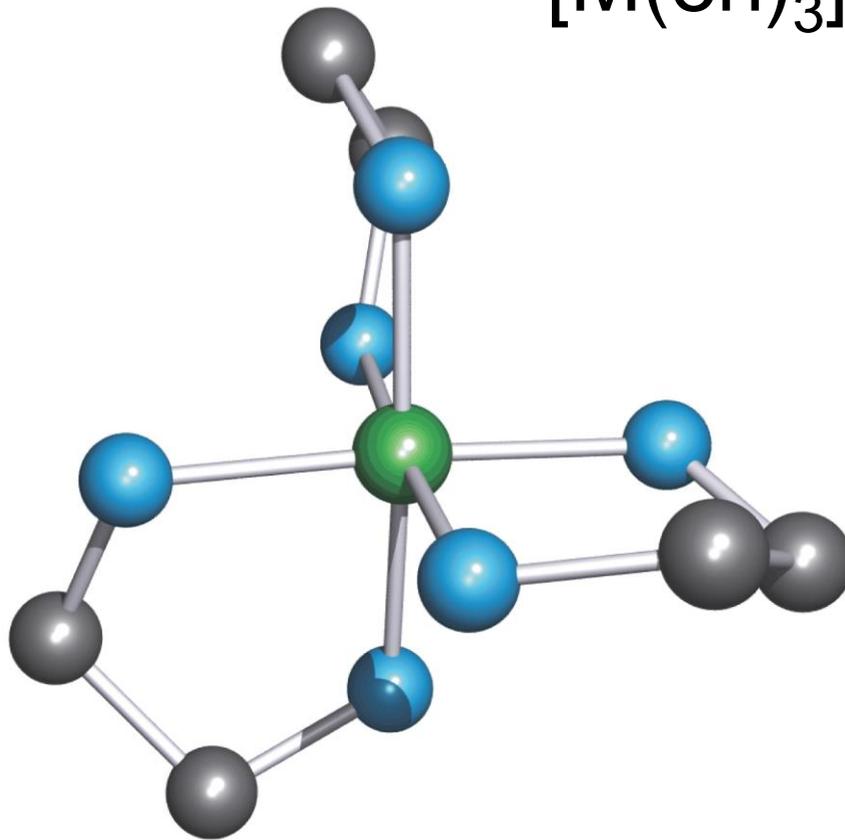
[†] The older names (still in use) for 1,2-ethanediamine, 1,4,7-triazaheptane and 1,4,7,10-tetraazadecane are ethylenediamine, diethylenetriamine and triethylenetetramine.

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	

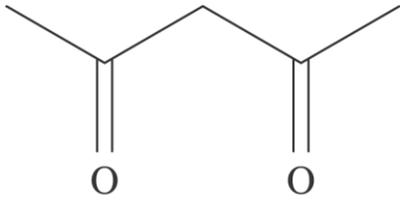
Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
1,10-Phenanthroline	phen	Bidentate	
1,4,7-Triazaheptane [†]	dien	Tridentate	
1,4,7,10-Tetraazadecane [†]	trien	Tetradentate	
<i>N,N,N',N'</i> -Ethylenediaminetetraacetate ion [‡]	[EDTA] ⁴⁻	Hexadentate	See equation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

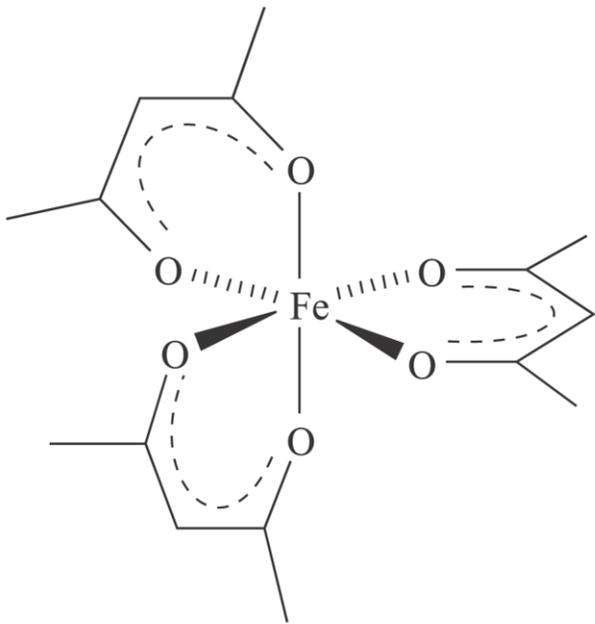
[‡] Although not systematic by the IUPAC rules, this is the commonly accepted name for this anion.



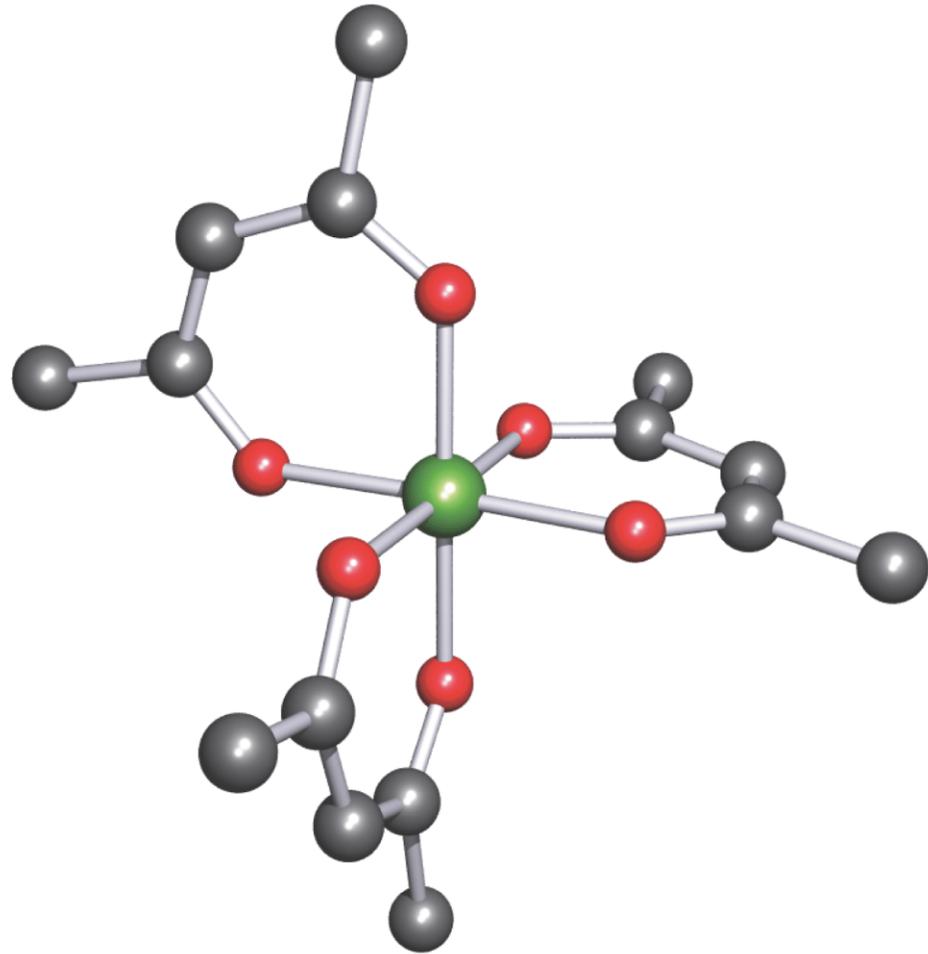
Anelli chelati a 5 termini



(a)



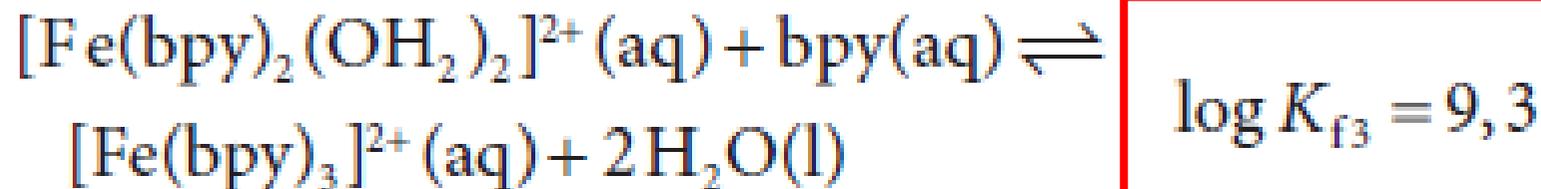
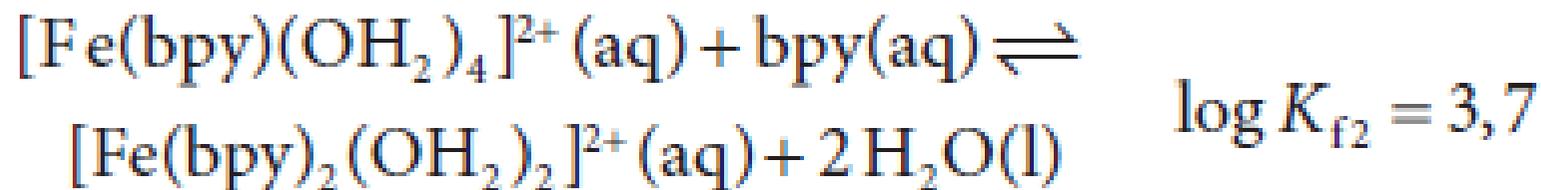
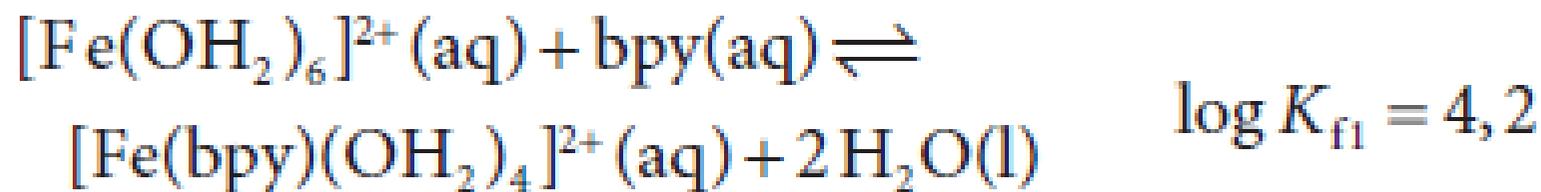
(b)

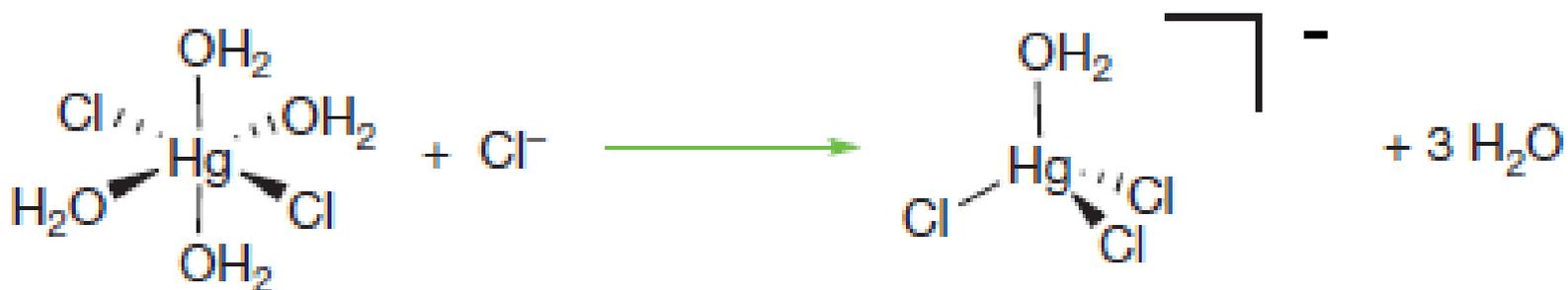
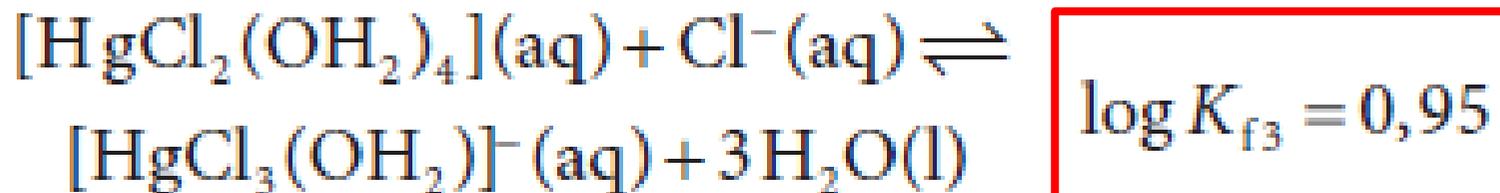
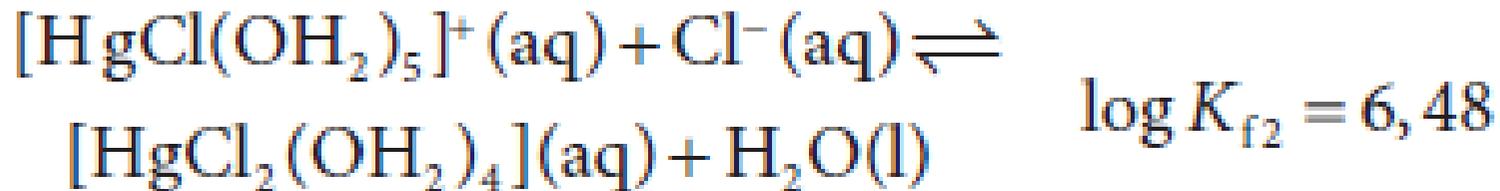
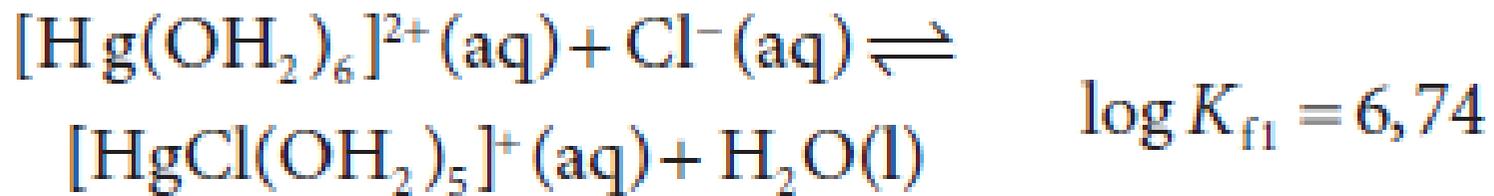


(c)

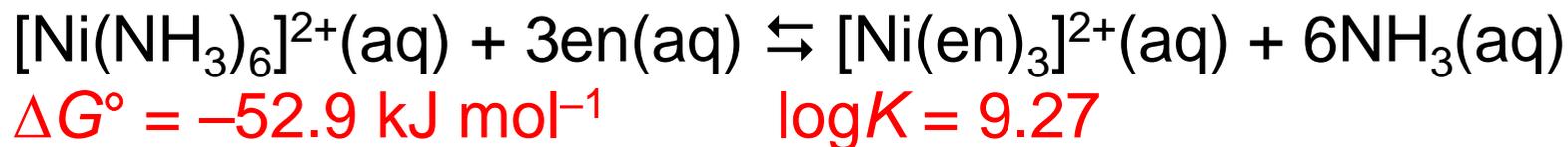
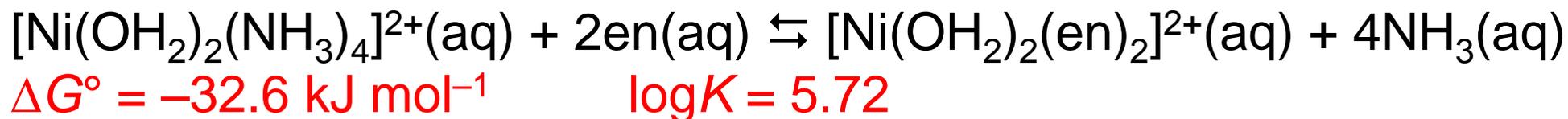
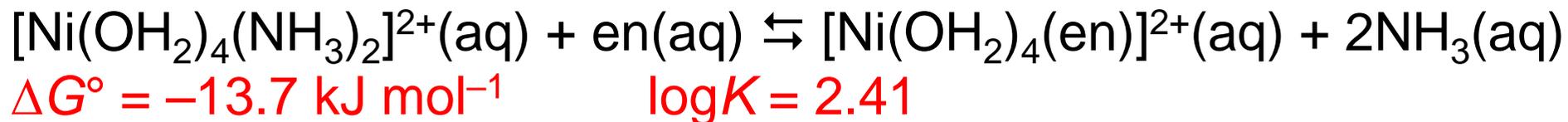
Anelli chelati a 6 termini

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

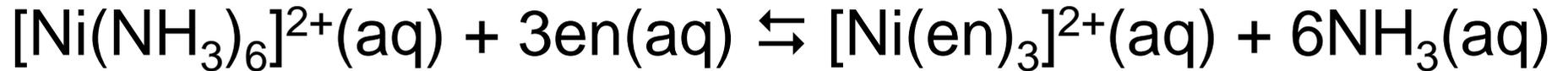




Effetto chelante



Effetto chelante



$$\log K = 9.27$$

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

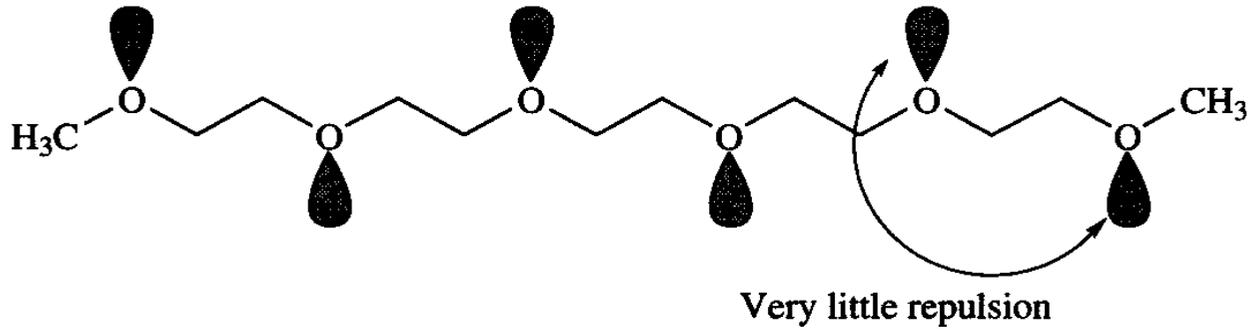
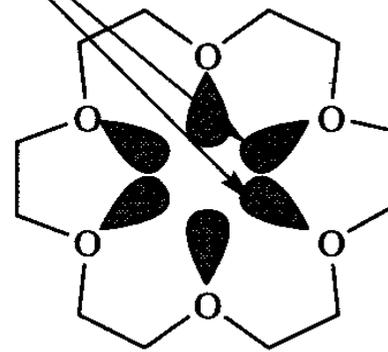
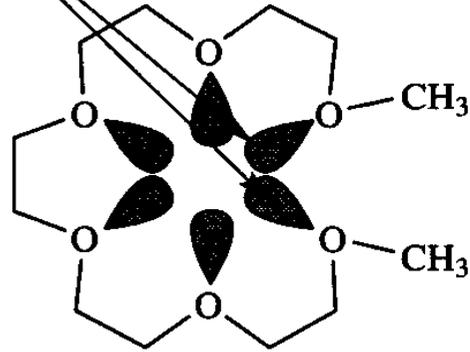
$$\Delta H^\circ = -16.8 \text{ kJ mol}^{-1}$$

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

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

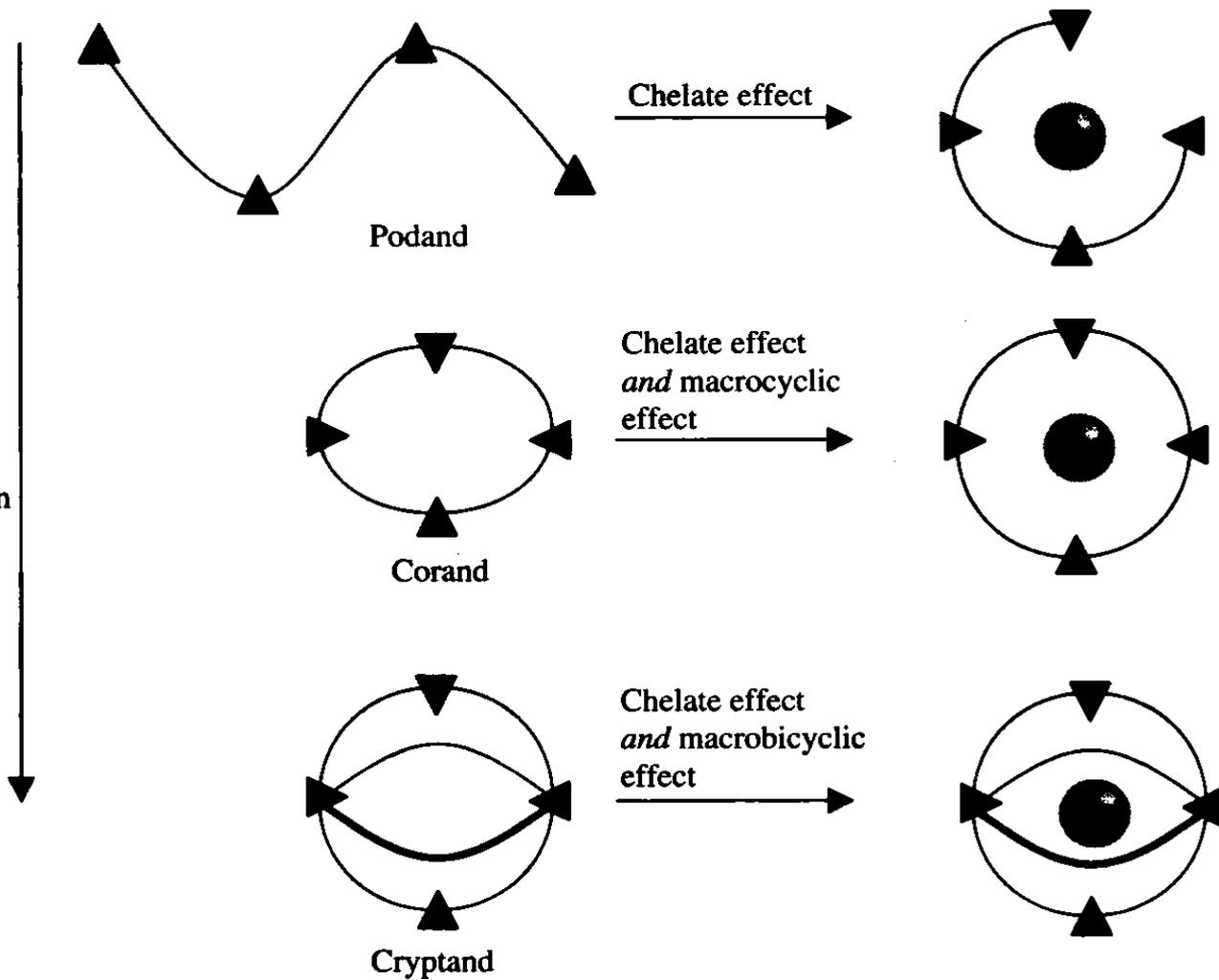
Effetto macrociclo

Lone pair-lone pair repulsive interaction



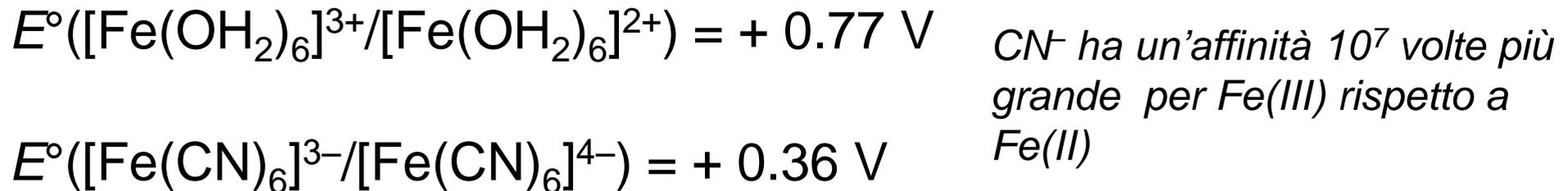
podando

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,*

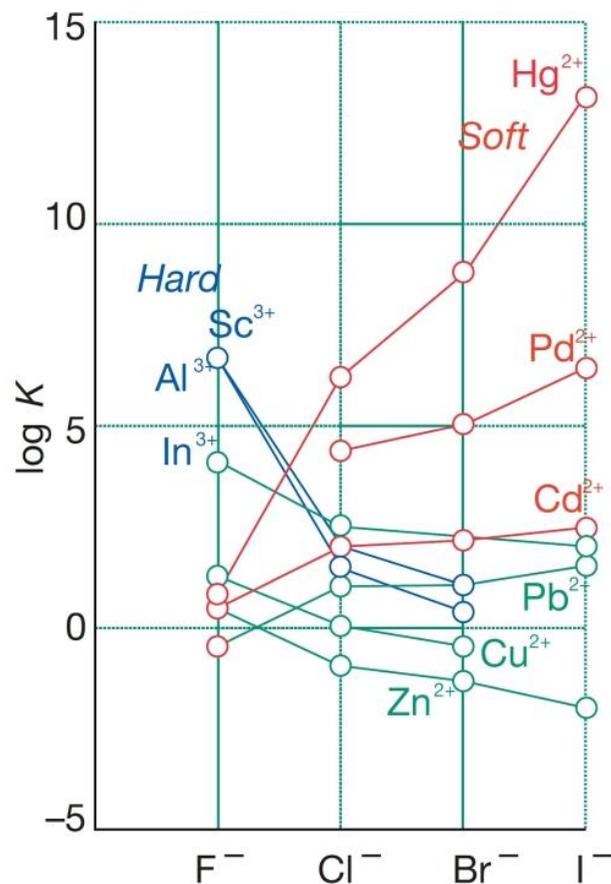
Influenza della complessazione sul potenziale standard di uno ione metallico M

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

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

Costanti di formazione di ioni metallici con alogenuri

Metal ion	log K_1			
	X = F	X = Cl	X = Br	X = I
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



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)	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*