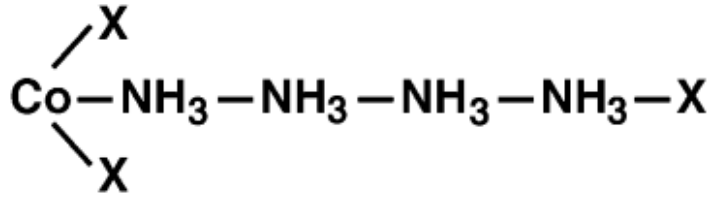
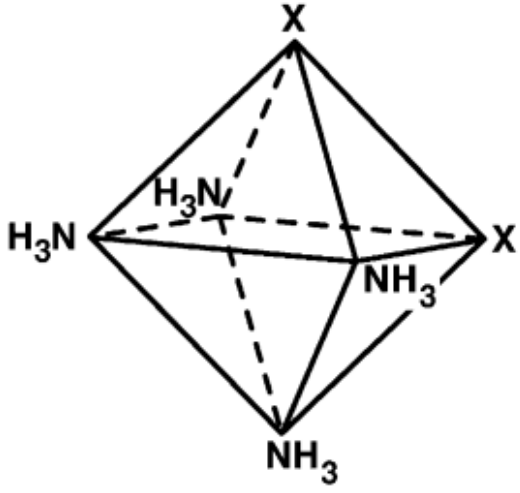
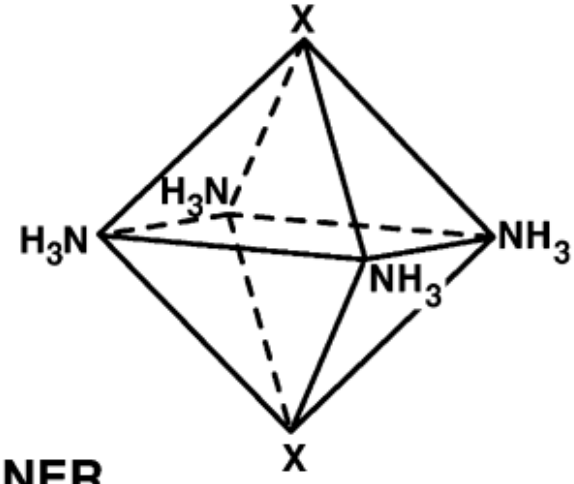
Alfred Werner 1866 – 1919
Premio Nobel per la chimica 1913

$CoCl_3 \cdot 6NH_3$	Giallo	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5NH_3$	Rosso-viola	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4NH_3$	Verde	$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4NH_3$	Violetto	

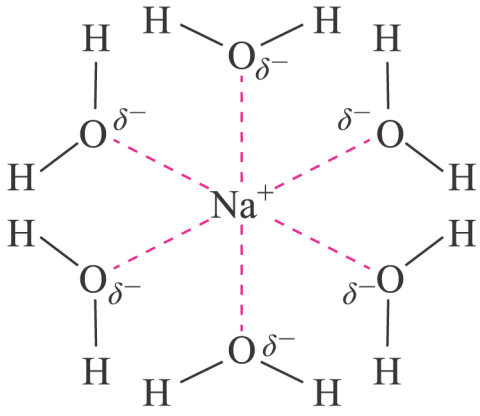


JØRGENSEN

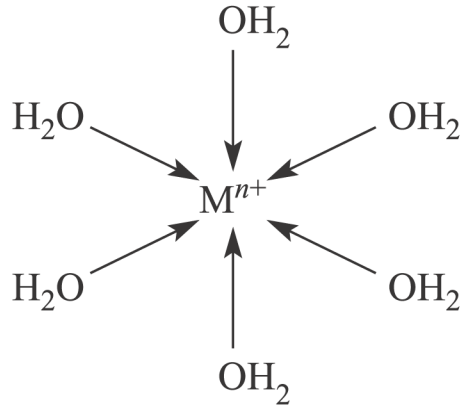




WERNER



(a)



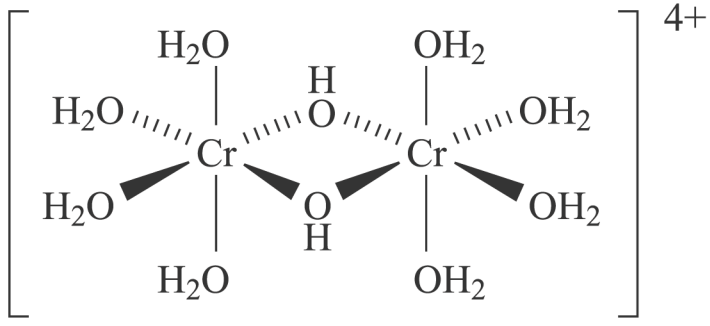
(b)

$M^{n+}(aq)$

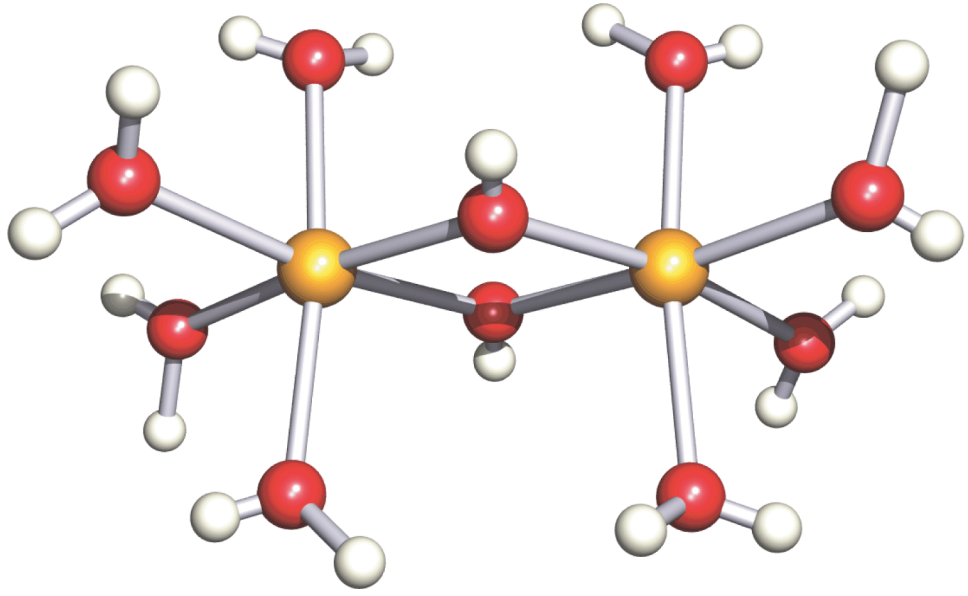
$[M(OH_2)_6]^{n+}$

pK_a $[Fe(OH_2)_6]^{3+}(aq) = 2.0$

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

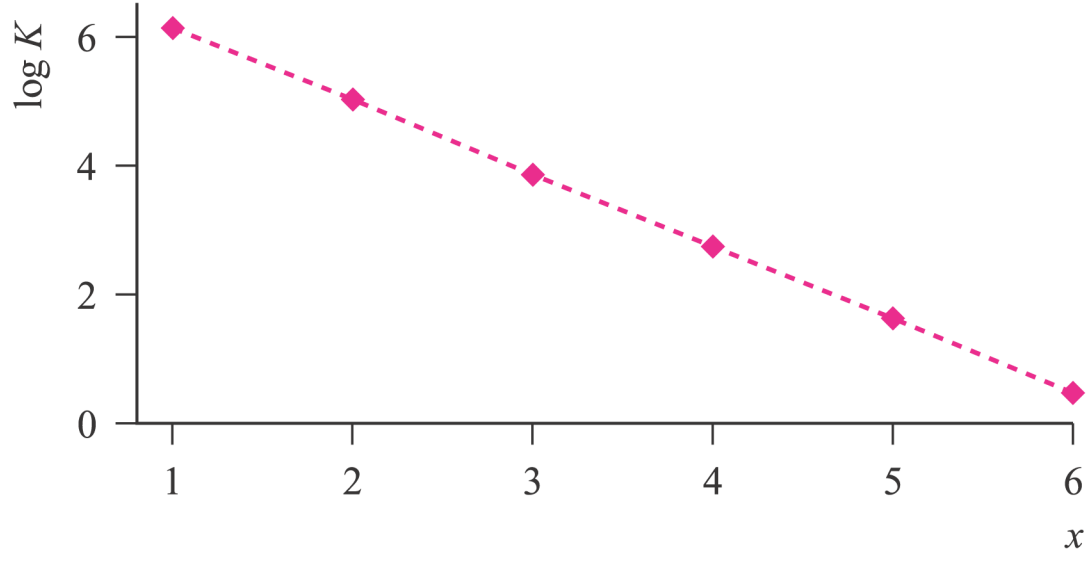


(a)



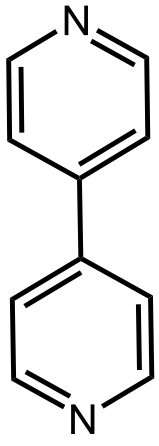
(b)

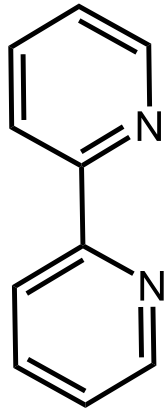
Costanti di stabilità parziali per la formazione di $[M(OH_2)_{6-x}L_x]^{n+}$

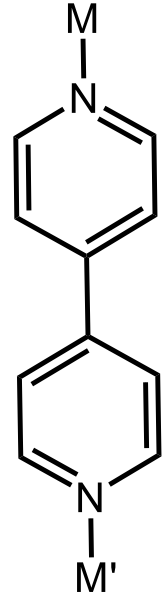


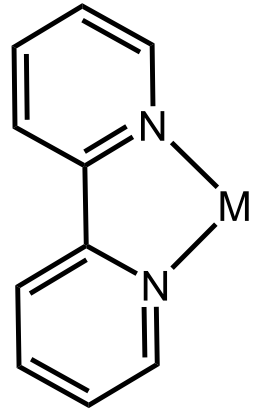
$$\beta = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6$$

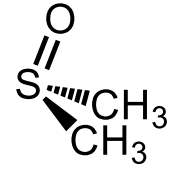
- Leganti politopici
- Leganti polidentati (chelanti)
- Leganti ambidentati

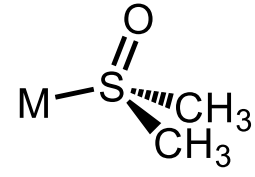


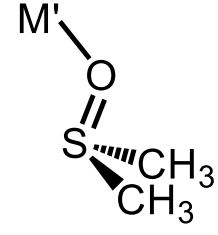


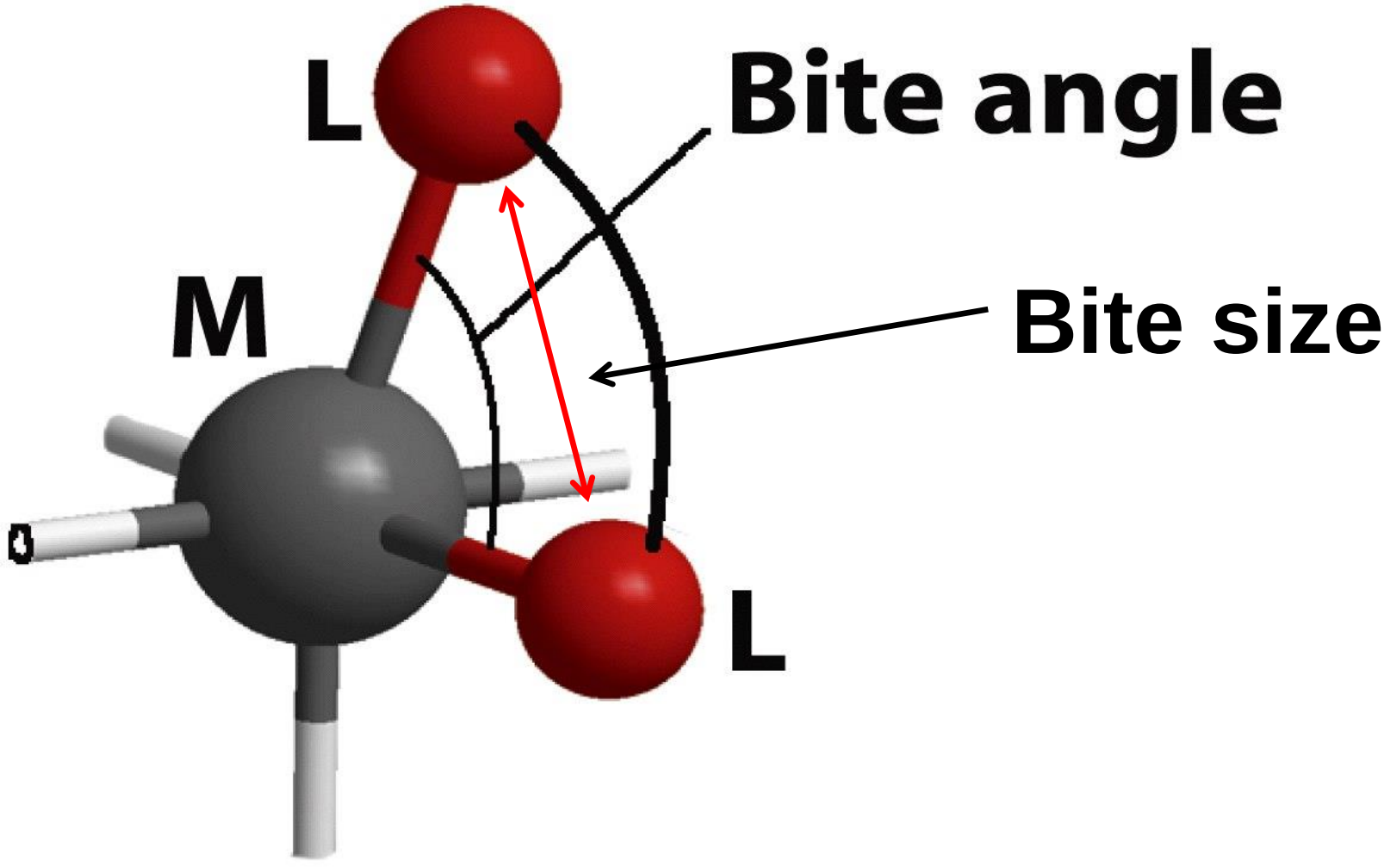


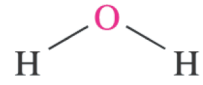
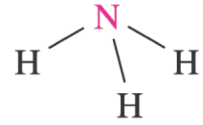
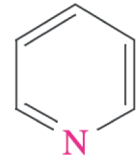
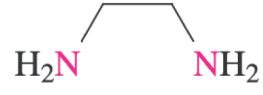




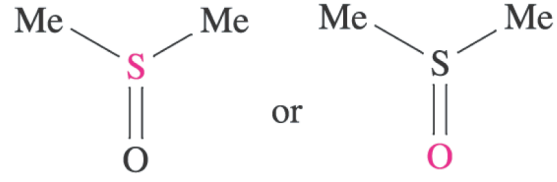
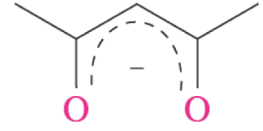
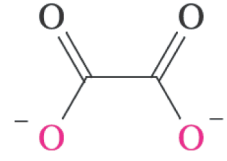
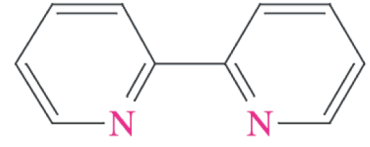


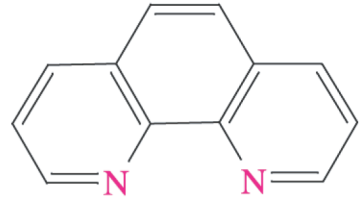
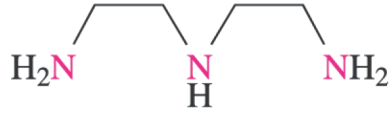



L
Bite angle
M
Bite size
L

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.

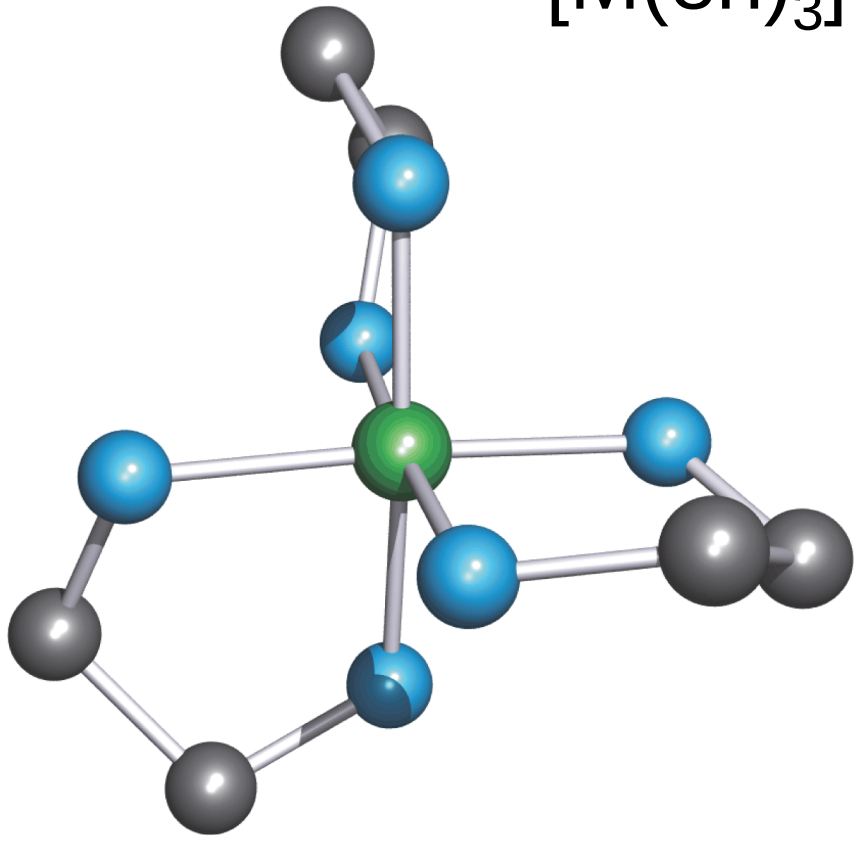
Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
Dimethylsulfoxide	DMSO	Monodentate	
Acetylacetonate ion	$[acac]^-$	Bidentate	
Oxalate or ethanedioate ion	$[ox]^{2-}$	Bidentate	
2,2'-Bipyridine	bpy or bipy	Bidentate	

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	
N,*N*,*N*',*N*'-Ethylenediaminetetraacetate ion[‡]	$[EDTA]^{4-}$	Hexadentate	See equation 7.75

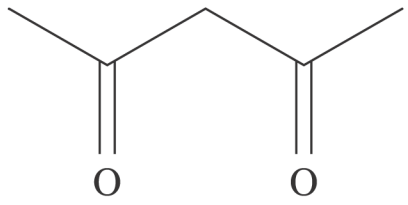
[†] The older names (still in use) for 1,2-ethanediamine, 1,4,7-triazaheptane and 1,4,7,10-tetraazadecane are ethylenediamine, diethylenetriamine and triethylenetetramine.

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

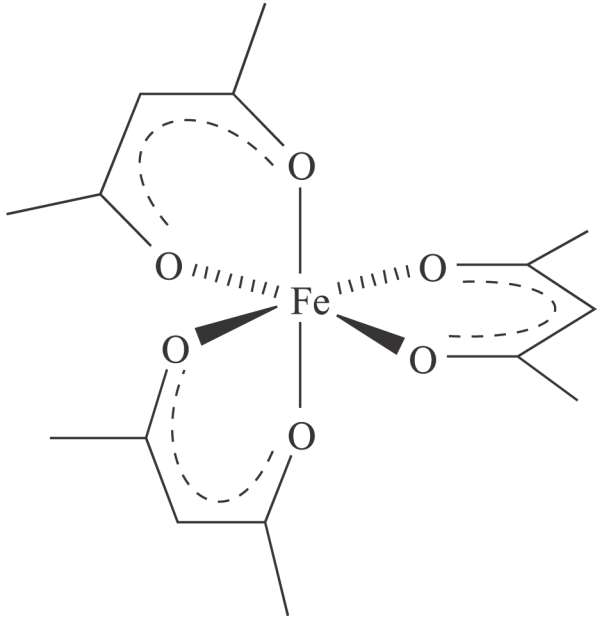
$[M(en)_3]^{n+}$



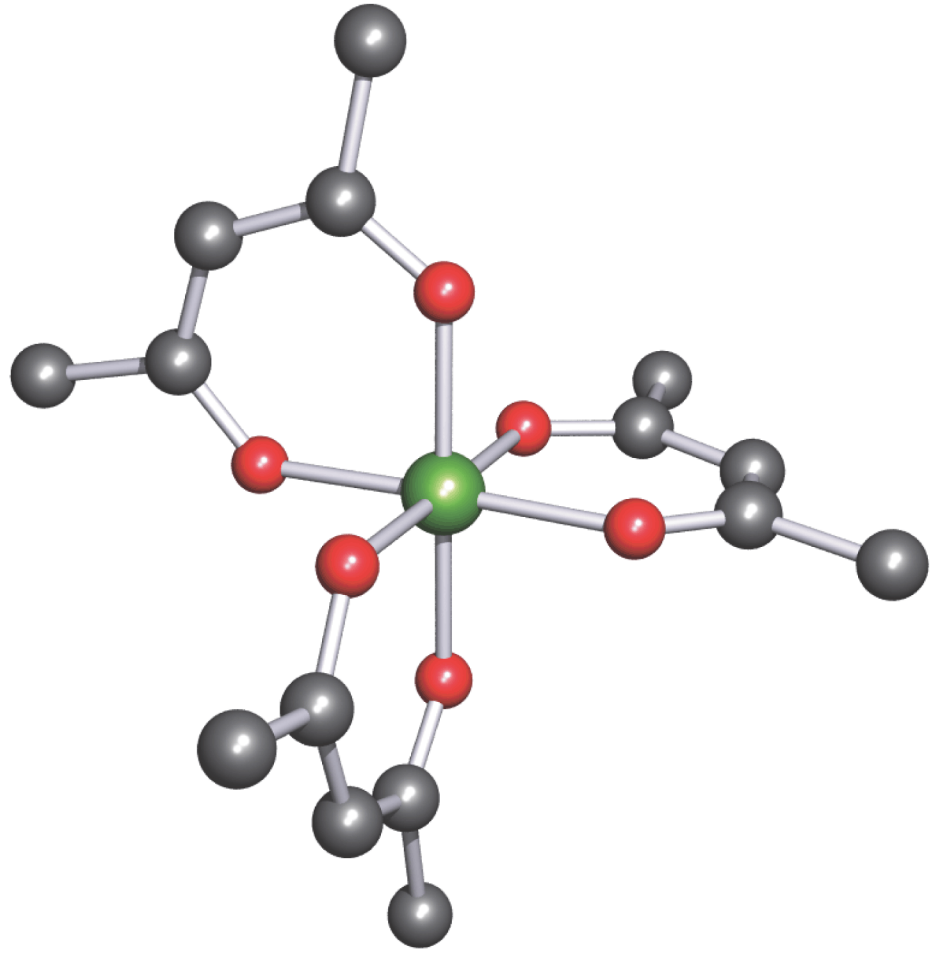
Anelli chelati a 5 termini



(a)



(b)



(c)

Anelli chelati a 6 termini

Effetto chelante

$$[Ni(NH_3)_6]^{2+}(aq) + 3en(aq) \leftrightarrows [Ni(en)_3]^{2+}(aq) + 6NH_3(aq)$$

$$\log K = 9.27$$

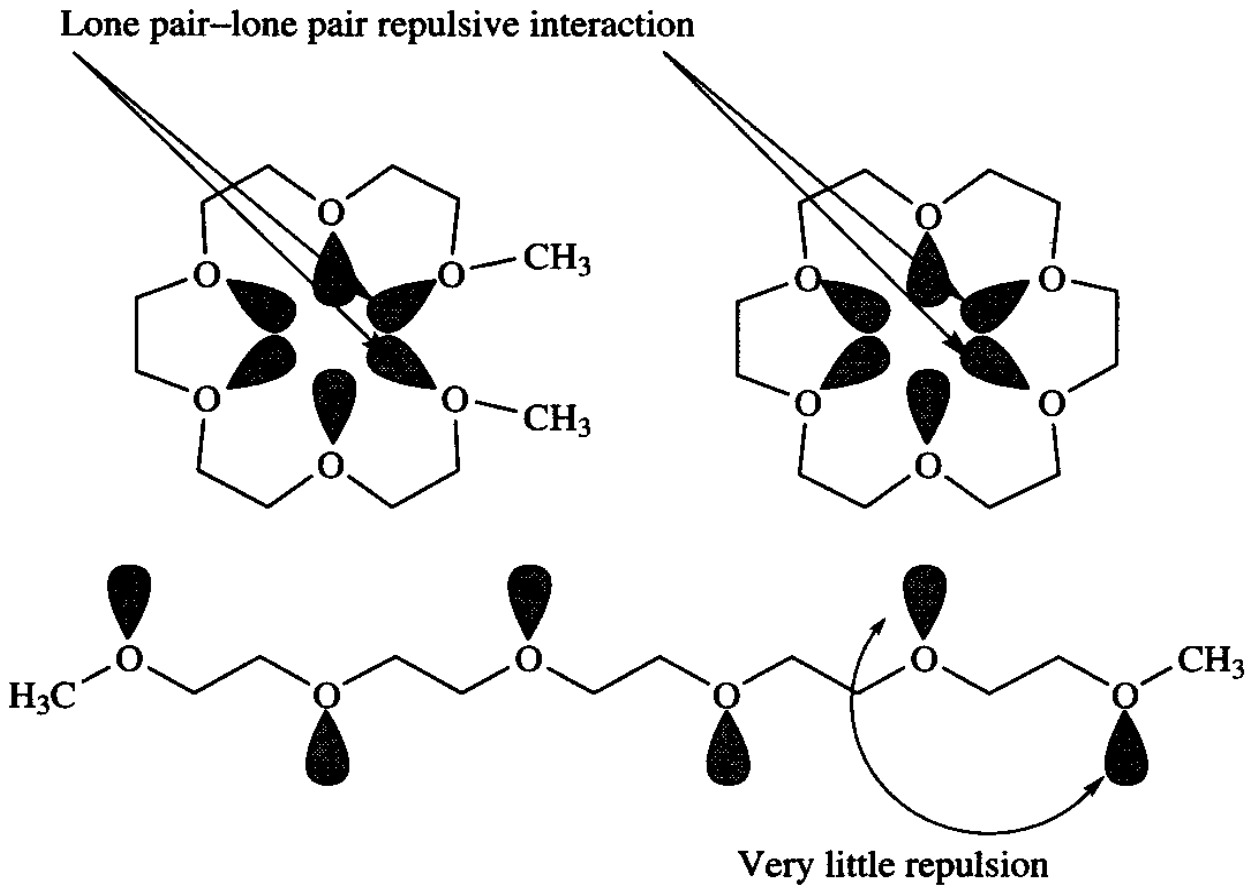
$$\Delta G° = -52.9 \text{ kJ mol}^{-1}$$

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

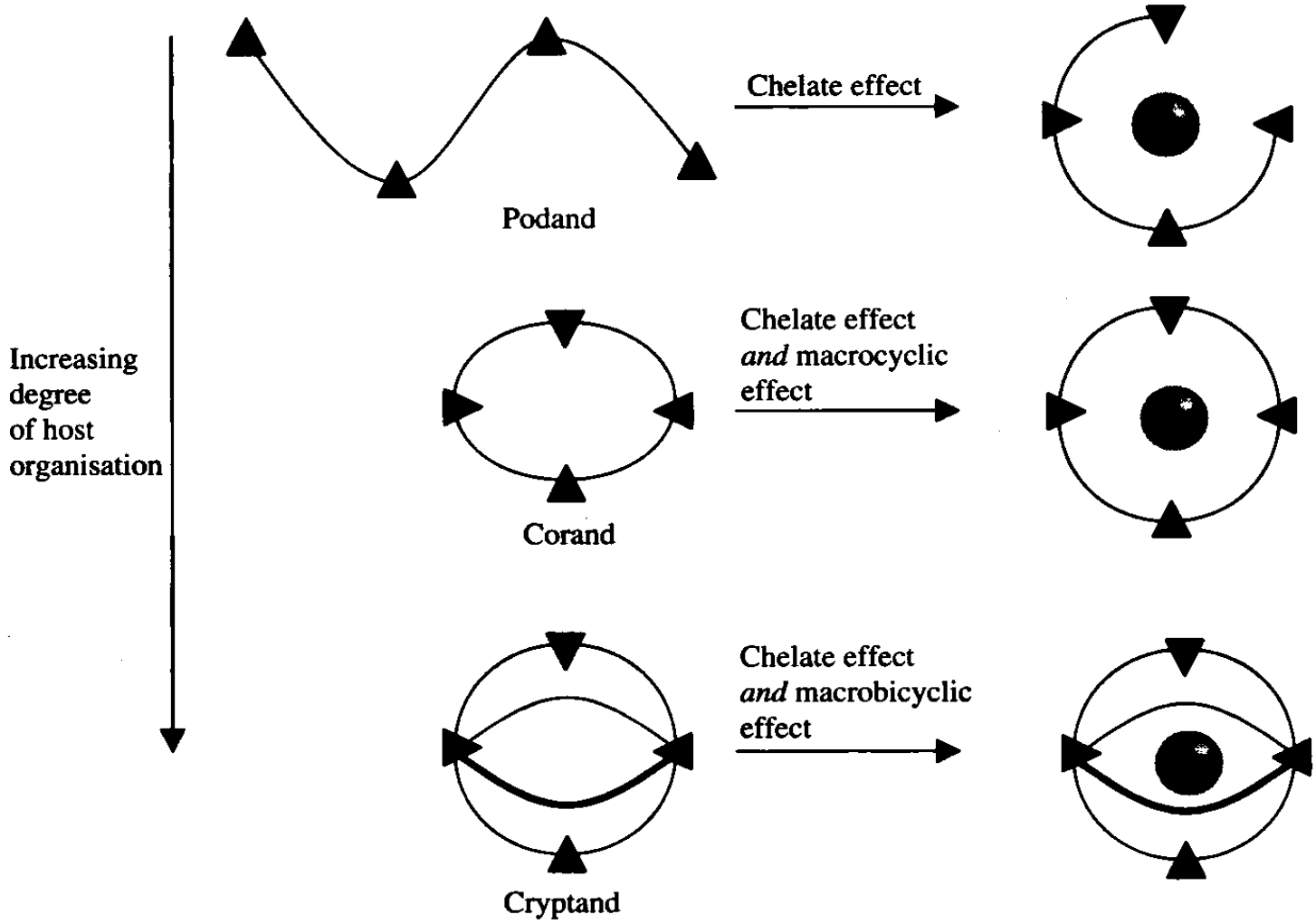
$$\Delta S° = +121 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

Effetto macrociclo



podando


Increasing
degree
of host
organisation
Podand
Chelate effect
Corand
Chelate effect
and macrocyclic
effect
Cryptand
Chelate effect
and macrobicyclic
effect

	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

elettronegatività

Hard *Soft*

HSAB principle
(*Pearson*)

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+}, $[VO]^{2+}$, $[VO_2]^+$
Soft; class (b)	Zero oxidation state metal centres, Tl^+, Cu^+, Ag^+, Au^+, $[Hg_2]^{2+}$, 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^-, $[CN]^-$ (*C*-bound), CO (*C*-bound), RNC, RSH, R_2S, $[RS]^-$, $[SCN]^-$ (*S*-bound), R_3P, R_3As, R_3Sb, alkenes, arenes
Intermediate	Br^-, $[N_3]^-$, py, $[SCN]^-$ (*N*-bound), $ArNH_2$, $[NO_2]^-$, $[SO_3]^{2-}$