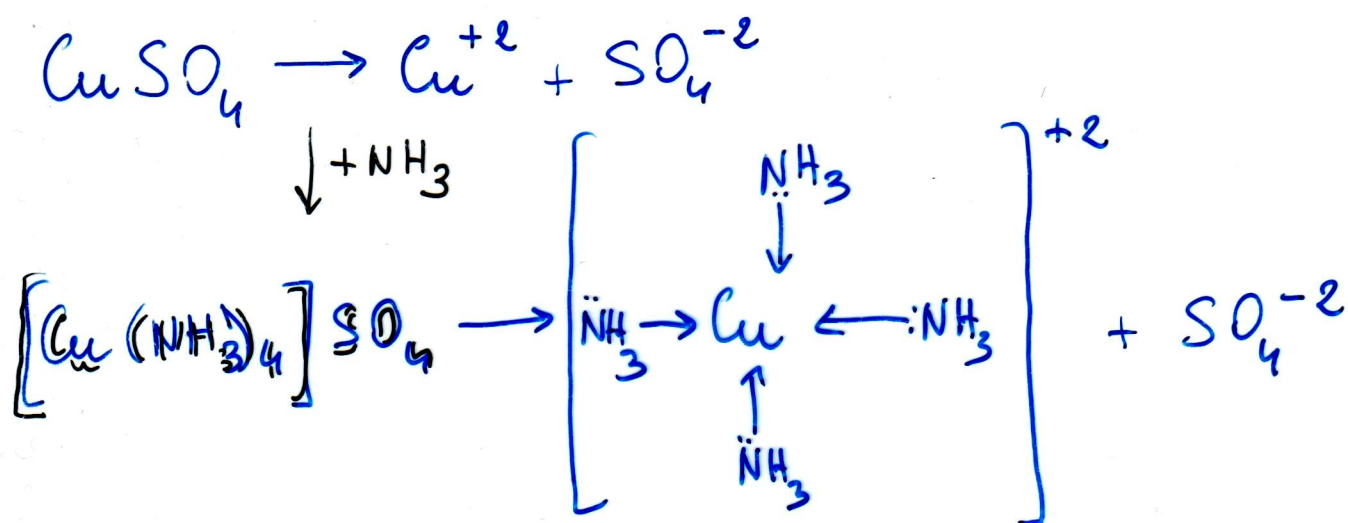


COMPOSTI DI COORDINAZIONE (Complessi)



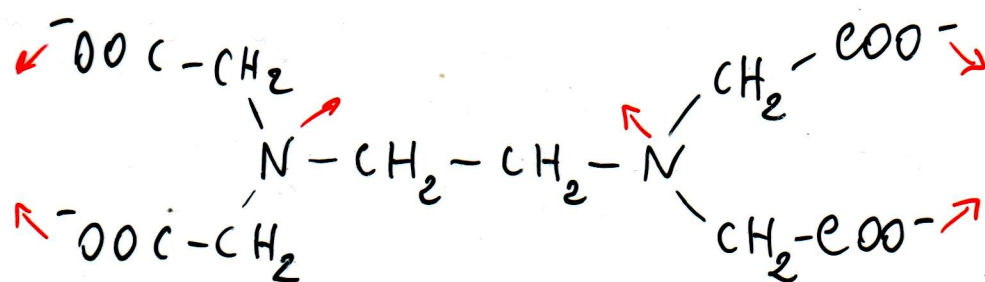
LIGANDI: donatori di una coppia di elettroni.
Possono essere **neutri** o **anionici**, ma sempre con una coppia di elettroni disponibili (lone pairs)
neutri: NH_3 , CO , NO , H_2O

anionici: CN^- , F^- , Cl^- , I^- , Br^- , OH^- , NO_2^- , NO_3^-

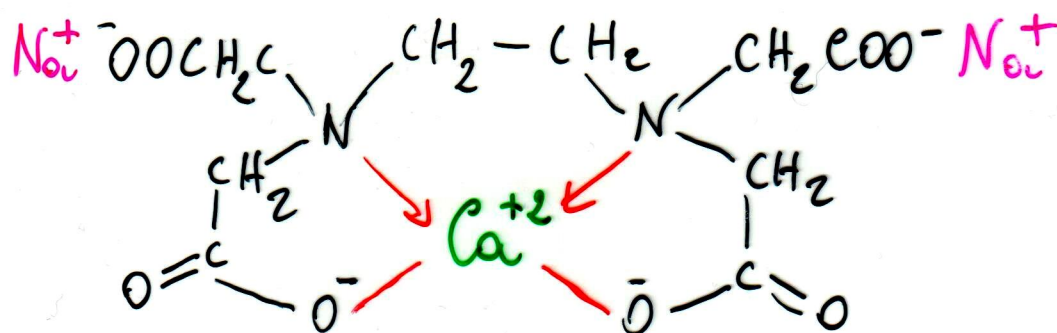
METALLI: i cationi che sono migliori accettori di elettroni sono quelli con: 1) **alta carica** (+2, +3, +4); 2) **piccolo raggio ionico**; 3) **orbitali esterni non completamente pieni**

↳ ioni dei **METALLI DI TRANSIZIONE**

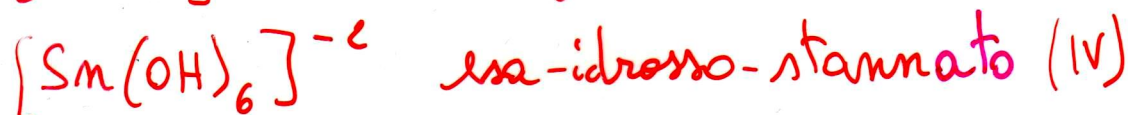
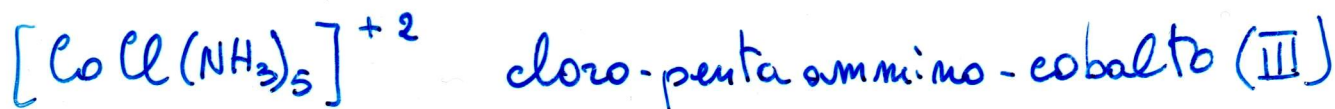
$$\text{potenziale ionico} = \frac{\text{carica}}{\text{raggio ionico}} = > 1.5$$



EDTA



EDTA - Na - Ca



catione

potenziale
ionico

Rb⁺

0.67

K⁺

0.75

Na⁺

1.05

Ba⁺²

1.48

Hg⁺²

1.80

Ca⁺²

2.00

Cd⁺²

2.00

Cu⁺

2.00

Mn⁺²

2.50

Fe⁺²

2.60

Zn⁺²

2.70

Co⁺²

2.80

Ni⁺²

2.90

Cu⁺²

2.80

Cr⁺³

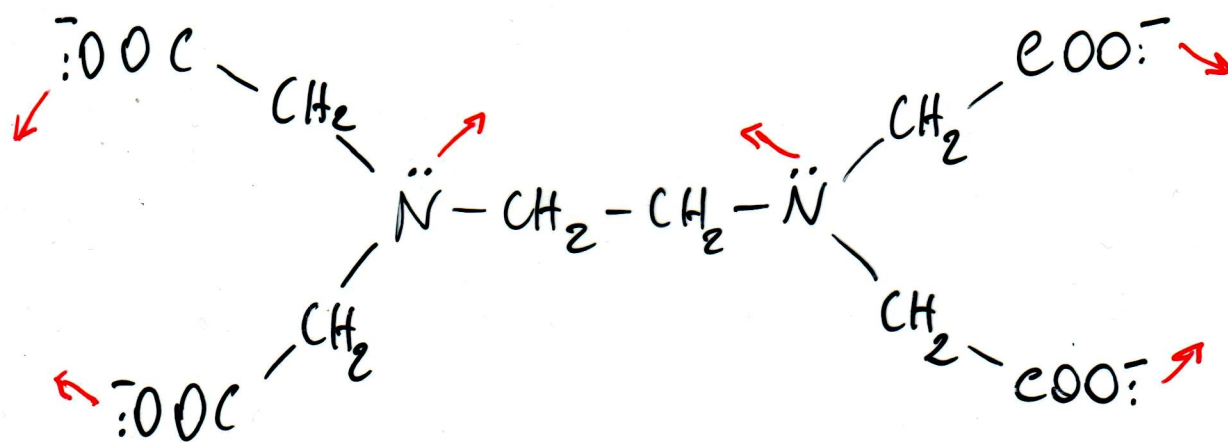
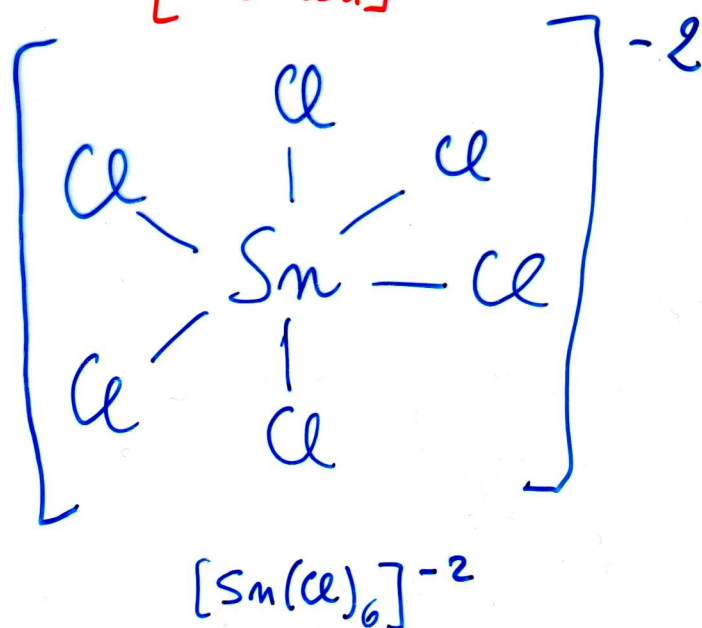
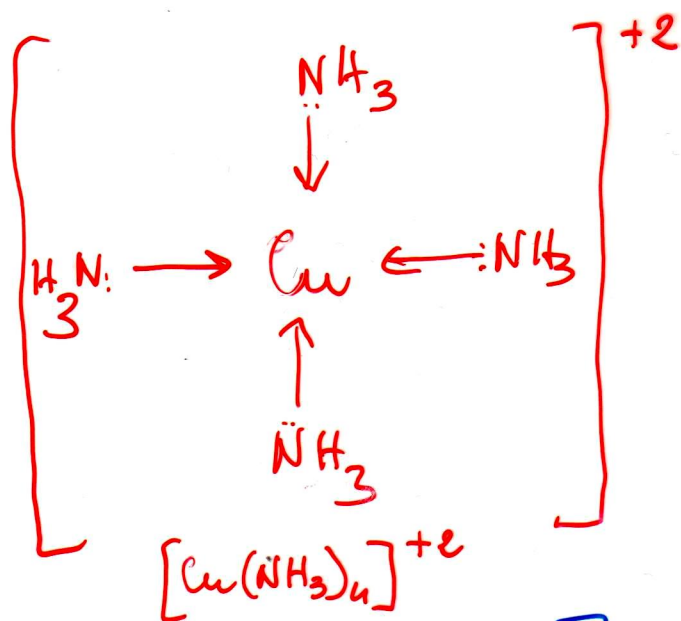
4.70

Fe⁺³

5.60

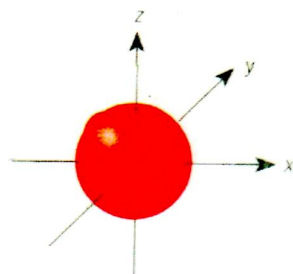
Al⁺³

6.00

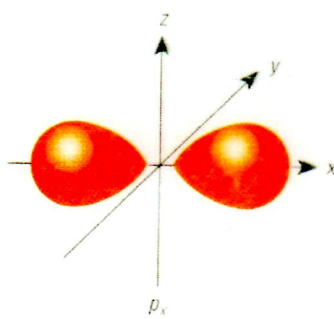


EDTA

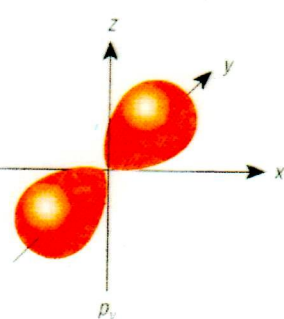
Acido EtilenDiamminoTetraacetico



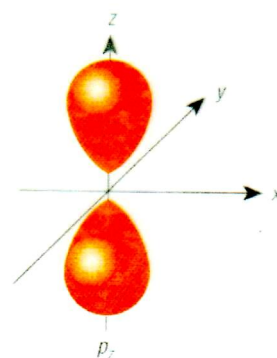
1) Orbitale s



p_x

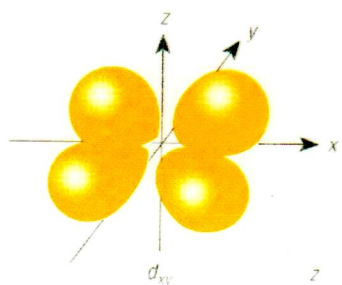


p_y

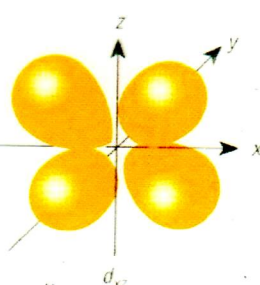


p_z

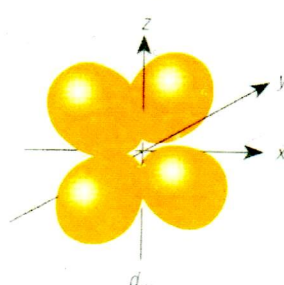
2) I tre orbitali p



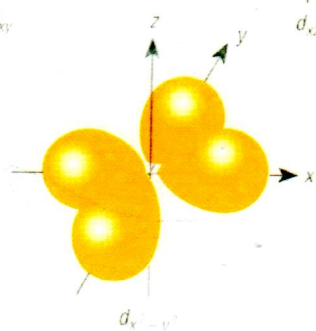
d_{xy}



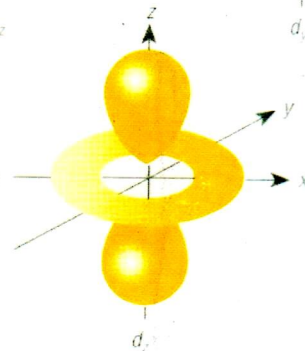
d_{xz}



d_{yz}



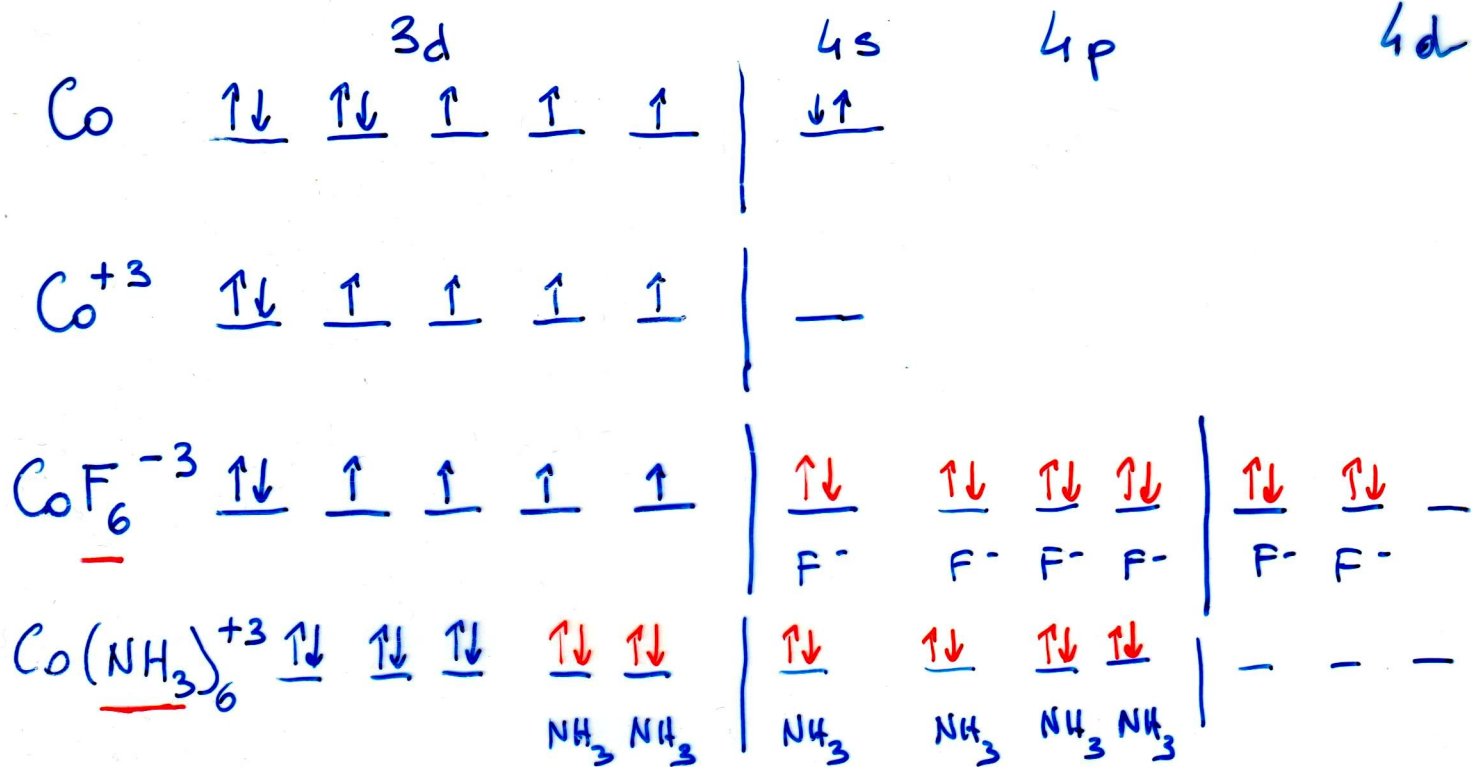
$d_{x^2-y^2}$



d_{z^2}

3) I cinque orbitali d

1. TEORIA DEL LEGAME DI VALENZA

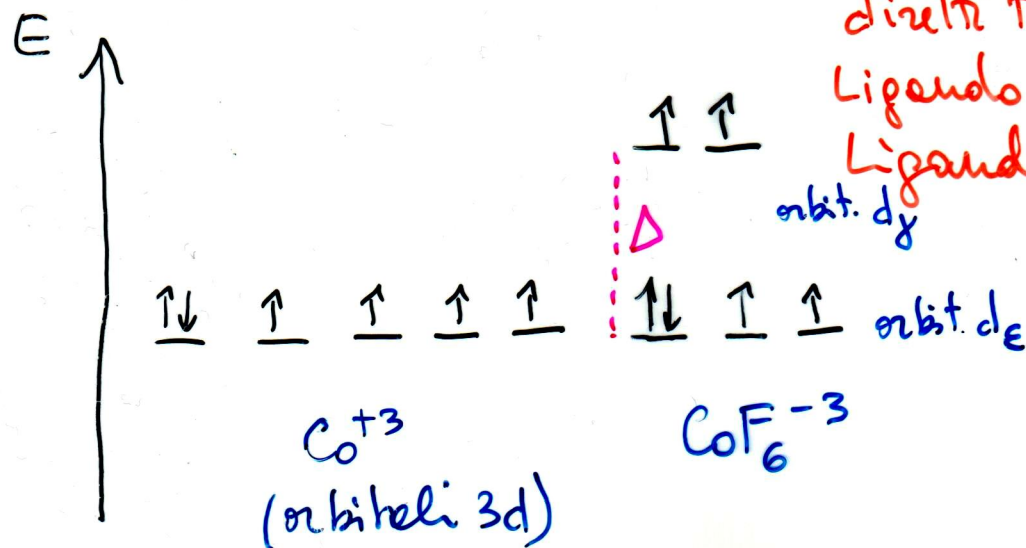
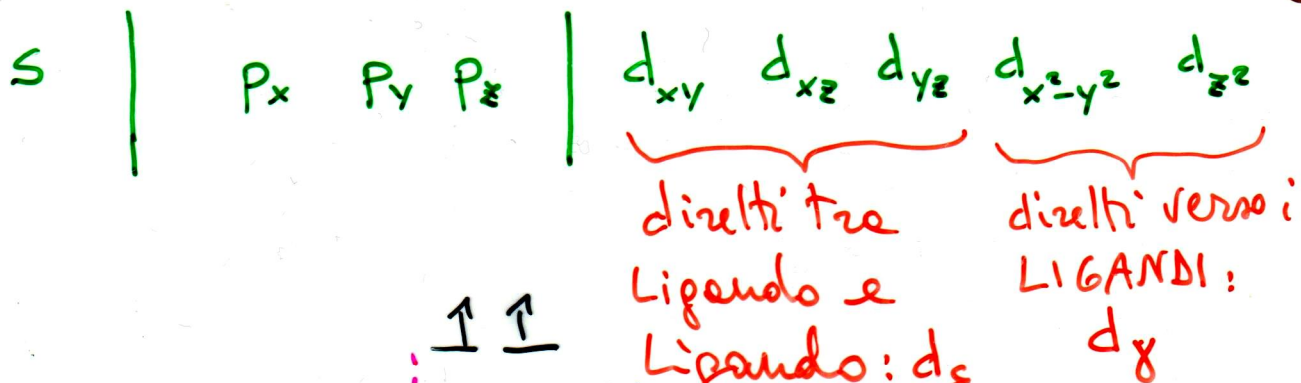


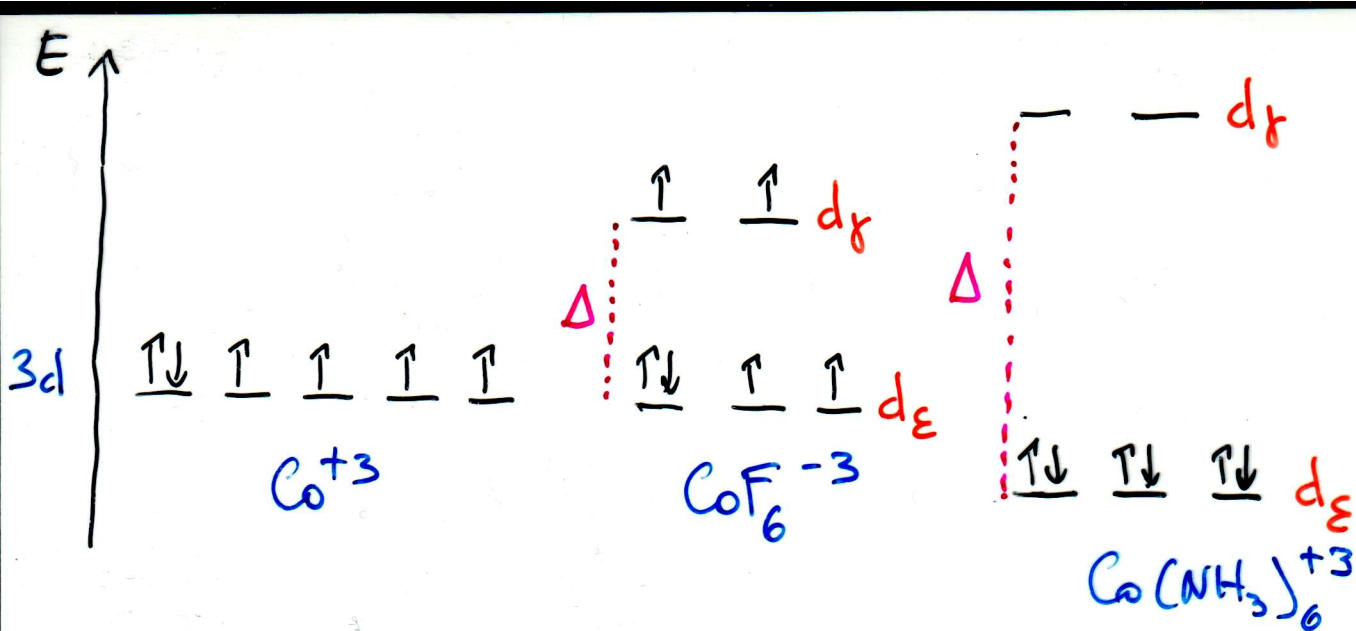
CoF₆⁻³ : ibridi $sp^3d^2 \rightarrow$ complesso esterno

Co(NH₃)₆⁺³ : ibridi $d^2sp^3 \rightarrow$ complesso interno

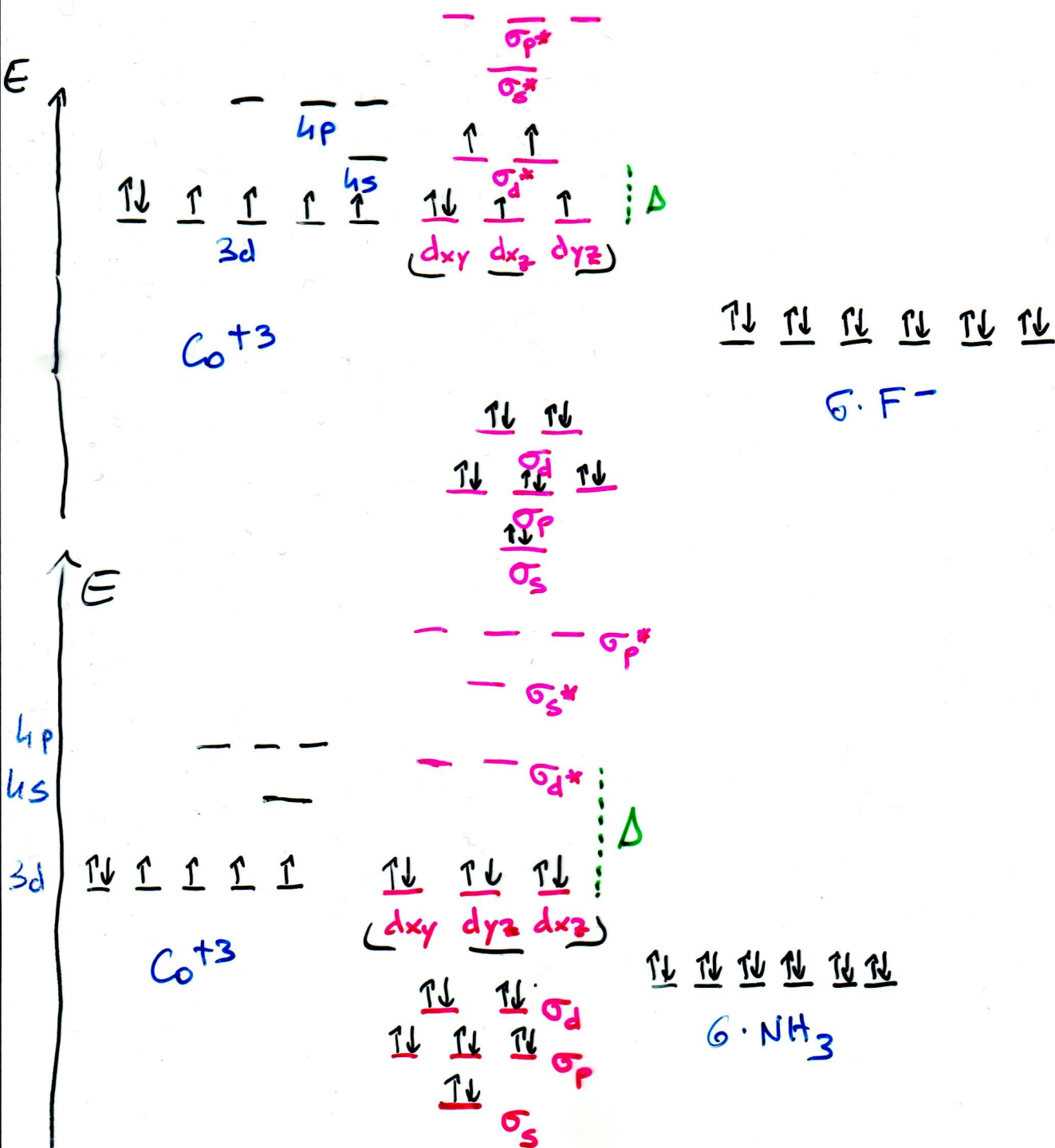
CoF₆⁻³ : paramagnetico Co(NH₃)₆⁺³ : diamagnetico

2. TEORIA DEL CAMPO CRISTALLINO OD ELETTROSTATICO



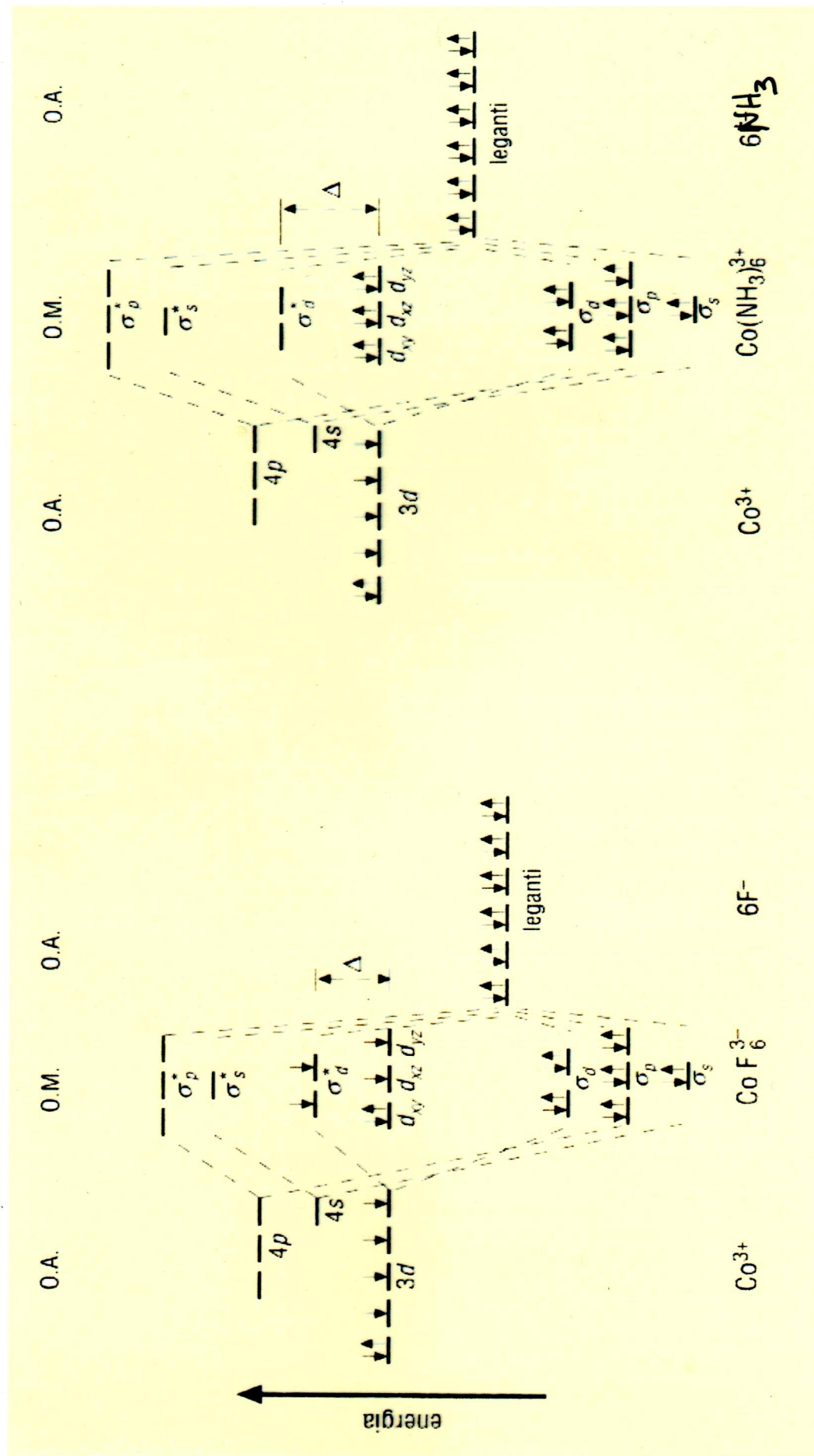


3. TEORIA DEGLI ORBITALI MOLECOLARI

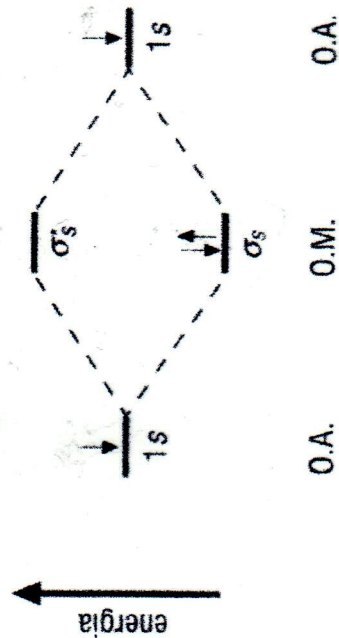




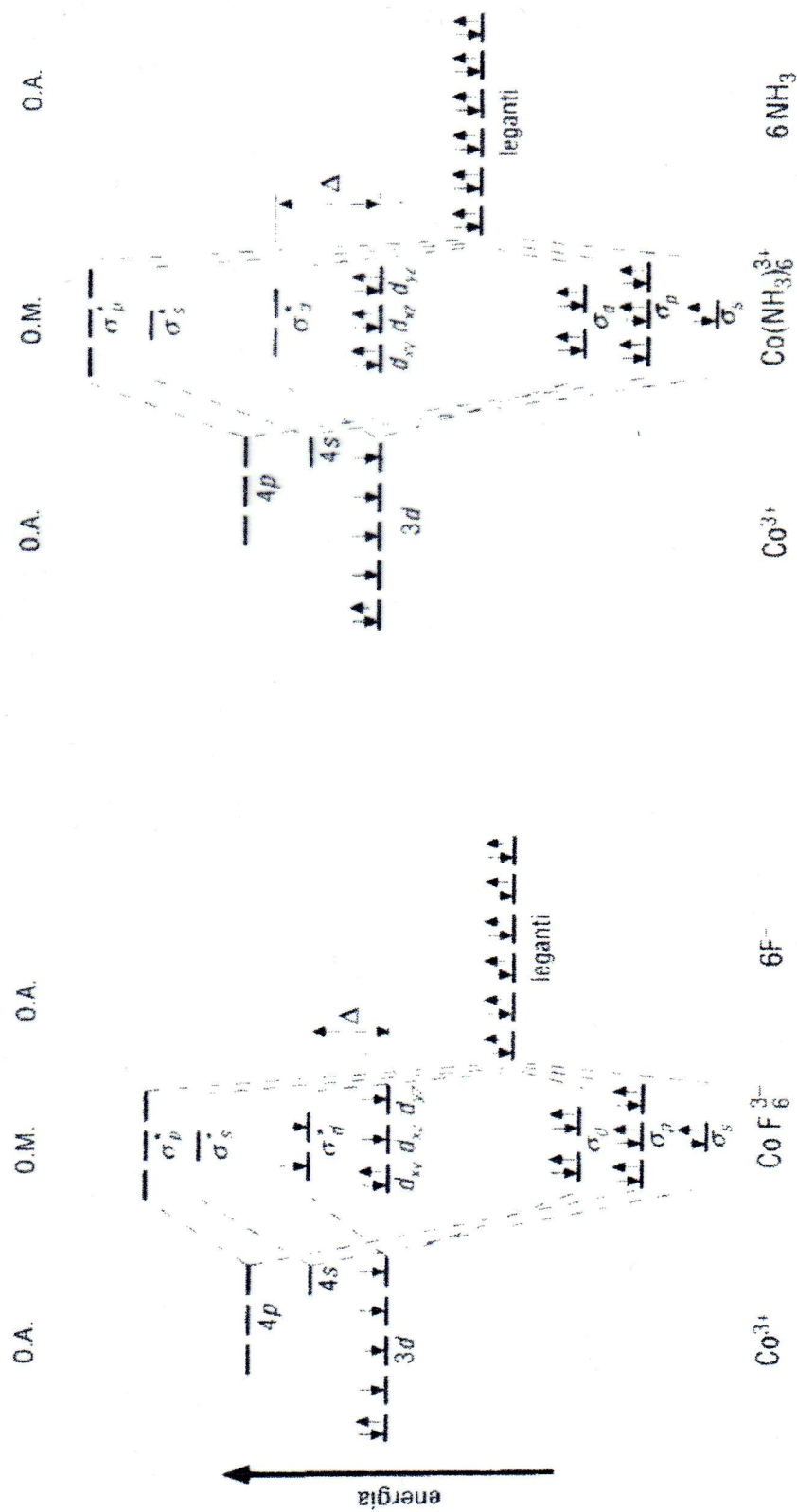
elettrostatico in complessi di Co(III) ad alto spin e a basso spin



GLI ORBITALI MOLECOLARI PER I COMPLESSI
 CoF_6^{3-} E $\text{Co(NH}_3)_6^{3+}$



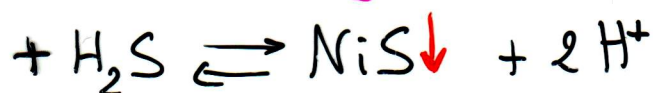
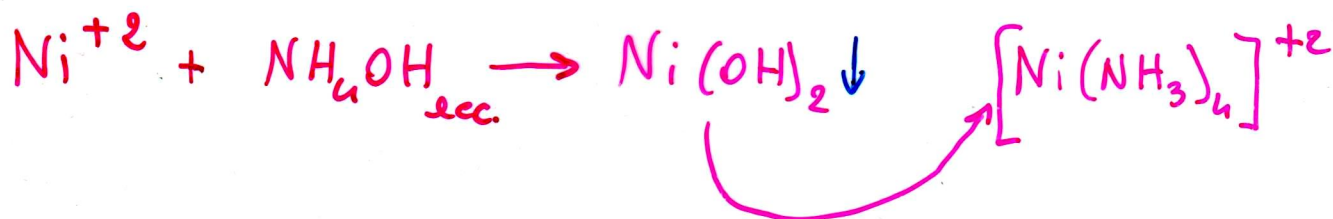
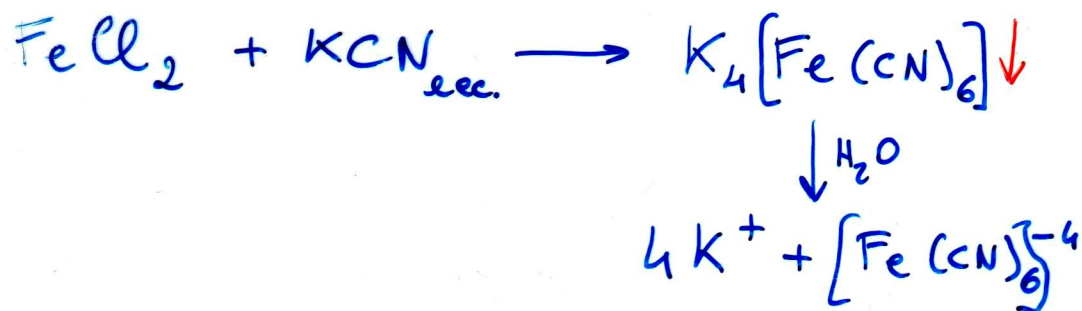
Orbitali molecolari (O.M.) per la molecola di idrogeno.



Gli orbitali molecolari per i complessi CoF_6^{3-} e $\text{Co}(\text{NH}_3)_6^{3+}$.

N° di coordinaz.	Geometria di coordinazione	Esempi	Ibridizzazione
2	- Lineare	Cu^{+2}, Ag^{+}, Au^{+} Hg^{+2}	sp
3	- Trigonale piana - Piramidale	Cu^{+} $As^{+3}, Sb^{+3}, Bi^{+3}$	sp^2 sp^3
4	- Tetraedrica - Planare quadrata	Ni^{+2}, Pd^{+2} Pt^{+2}	sp^3 dsp^2
6	- Ottaedrica	$Ni^{+2}, Co^{+2}, etc...$	d^2sp^3 sp^3d^2

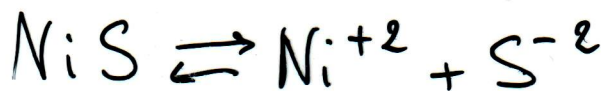
STABILITÀ DEI COMPLESSI





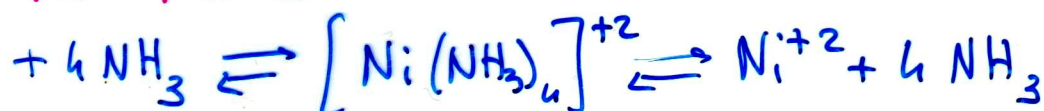
$$K_{ps} \underset{\text{Ni}(\text{OH})_2}{\approx} 10^{-15} = [\text{Ni}^{+2}] [\text{OH}^-]^2 = \Delta \cdot (2\Delta)^2 = 4\Delta^3$$

$$\Delta_{\text{Ni}(\text{OH})_2} \approx \sqrt[3]{\frac{10^{-15}}{4}} \approx 10^{-5} \text{ M}$$



$$K_{ps \text{ NiS}} \approx 10^{-20} = [\text{Ni}^{+2}] [\text{S}^{-2}] = \Delta^2$$

$$\Delta_{\text{NiS}} = \sqrt{K_{ps}} \approx 10^{-10} \text{ M}$$



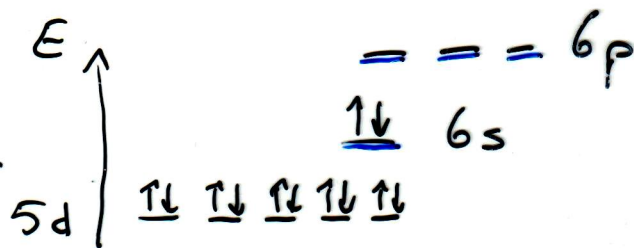
stabile rispetto all'idrossido

non stabile rispetto al solfuro

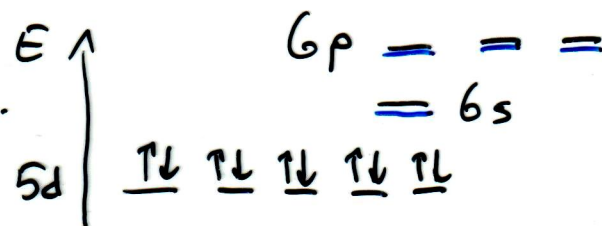
ESEMPIO DI FORMAZIONE DI UN COMPLESSO

Tra Hg^{+2} e Cl^-

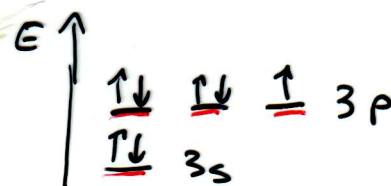
Hg^0 = configurat. elettr. est.
 $5d^{10} 6s^2$



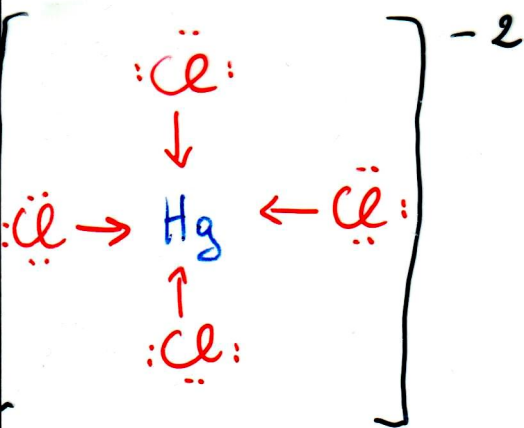
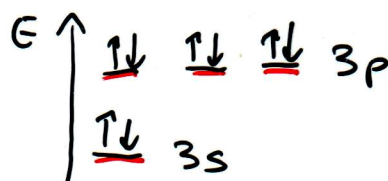
Hg^{+2}



Cl^0 = configurat. elettr. est.
 $3s^2 3p^5$



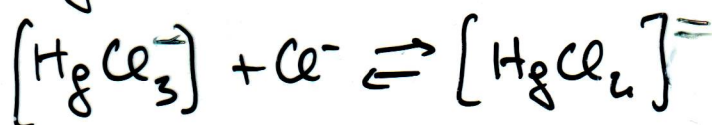
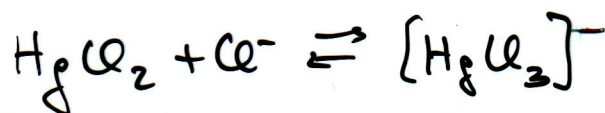
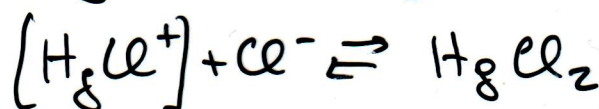
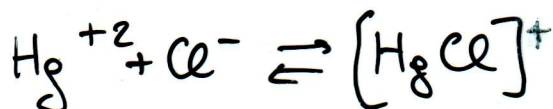
Cl^-



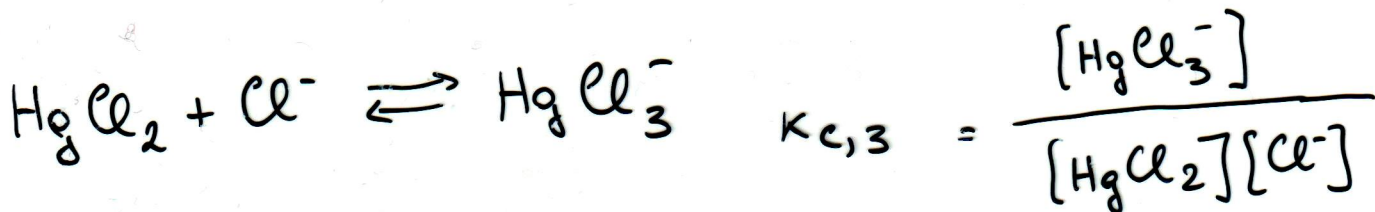
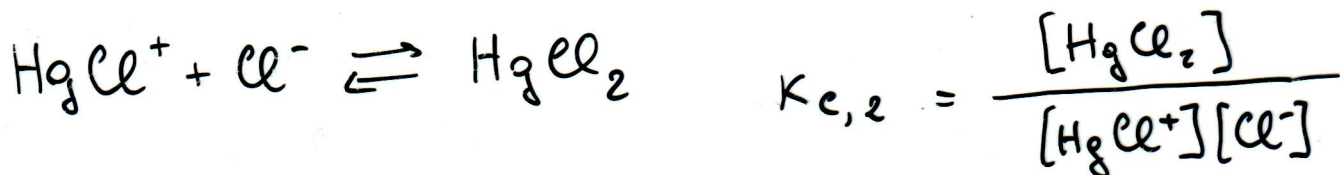
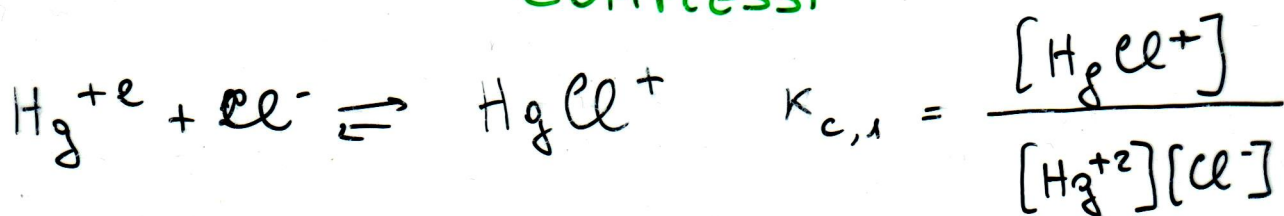
molecola a geometria tetraedrica

$$\chi_{\text{Hg}} = 1.5$$

$$\chi_{\text{Cl}} = 2.8$$



LA COSTANTE DI INSTABILITÀ DEI COMPLESSI



$K_{c,1-4}$ = COSTANTI DI STABILITÀ DEI COMPLESSI

$$\text{COSTANTI DI INSTABILITÀ} = \frac{1}{K_{\text{stab}}} = K_{\text{im}}$$

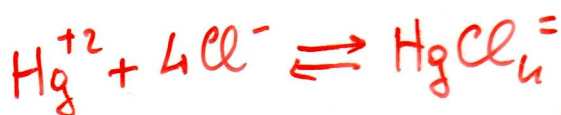
$$K_{\text{in},1} = \frac{[\text{Hg}^{+2}][\text{Cl}^-]}{[\text{HgCl}^+]}$$

$$K_{\text{in},2} = \frac{[\text{HgCl}^+][\text{Cl}^-]}{[\text{HgCl}_2]}$$

$$K_{\text{in},3} = \frac{[\text{HgCl}_2][\text{Cl}^-]}{[\text{HgCl}_3^-]}$$

$$K_{\text{in},4} = \frac{[\text{HgCl}_3^-][\text{Cl}^-]}{[\text{HgCl}_4^{2-}]}$$

$$K_{\text{in},1} \approx 10^{-7} ; K_{\text{in},2} \approx 10^{-7} ; K_{\text{in},3} \approx 10^{-1} ; K_{\text{in},4} \approx 10^{-1}$$



$$K_{\text{in,tot}} = \frac{[\text{Hg}^{+2}][\text{Cl}^-]^4}{[\text{HgCl}_4^{2-}]} = 10^{-16}$$

COME VARIA LA $[Me^{+m}]$ IN PRESENZA DI AGENTI COMPLESSANTI

Es. Consideriamo $Hg(NO_3)_2$ $c_s = 10^{-3} M$



1. LIGANDO IN FORTE ECCESSO: aggiungiamo una solut. di HCl $1 M$ ($pH=0$).

Consideriamo le incognite che abbiamo nell'eq.

incognite: $[Hg^{+2}]$, $[Cl^-]$, $[HgCl^+]$, $[HgCl_2]$, $[HgCl_3^-]$,

$[HgCl_4^{2-}]$, $[H^+]$; tuttavia $[H^+]$ e $[Cl^-]$ perchè molto superiori per la forte eccesso rispetto alle altre specie.

equazioni: $K_{in,1}$; $K_{in,2}$; $K_{in,3}$; $K_{in,4}$;

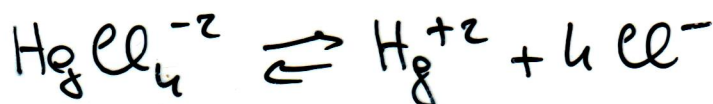
elettroneutralità:

$$2[Hg^{+2}] + [H^+] + [HgCl^+] = 2[NO_3^-] + [OH^-] + [HgCl_3^-] + 2[HgCl_4^{2-}]$$

conservazione specie $Hg^{+2} = 10^{-3} M$

conservazione specie $Cl^- = 1 M$

consideriamo la K_{in} totale:



$$K_{in_{TOT}} = \frac{[Hg^{+2}][Cl^-]^4}{[HgCl_4^{2-}]} \approx 10^{-16}$$

poiché il ligando è in forte eccesso ($\text{HCl } 1\text{M}$)
 il Hg^{+2} si può considerare TUTTO complessato
 come $[\text{HgCl}_4^{-2}]$:

$$[\text{HgCl}_4^{-2}] = \text{conc. iniz del } \text{Hg}^{+2} = 10^{-3} \text{ M}$$

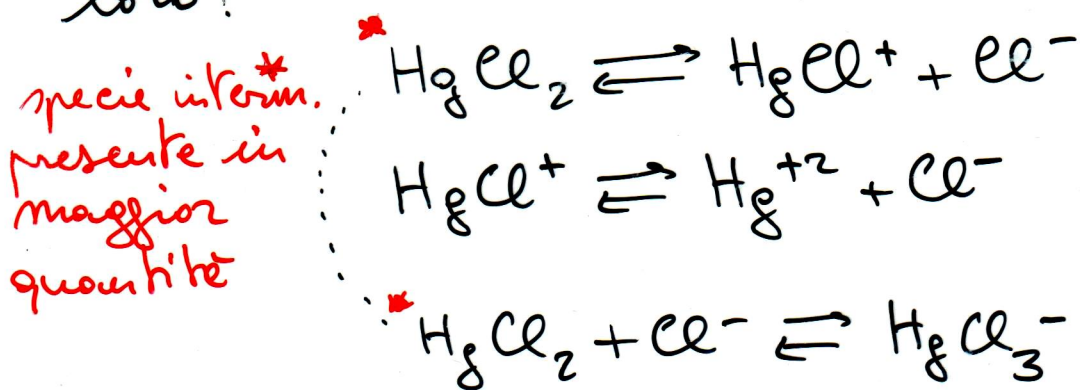
$$[\text{Cl}^-] = 1\text{M} \text{ (è diminuita in modo trascurabile)}$$

$$K_{\text{intot}} = \frac{[\text{Hg}^{+2}][\text{Cl}^-]^4}{[\text{HgCl}_4^{-2}]} = 10^{-16} = \frac{[\text{Hg}^{+2}] \cdot 1}{10^{-3}}$$

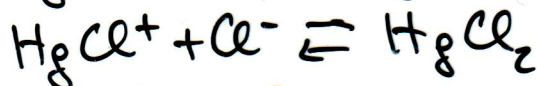
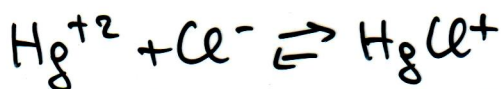
$$[\text{Hg}^{+2}] = 10^{-19} \text{ M}$$

2. LIGANDO AGGIUNTO NON IN ECCESSO

Ora le conc. dei complessi intermedi non sono
 più trascurabili, ma tutte paragonabili tra
 loro:



conc. iniz. $\text{Hg}^{+2} = 10^{-1} \text{ M}$; aggiungiamo $\text{HCl } 10^{-1} \text{ M}$



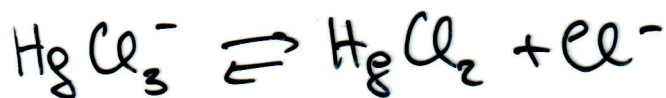
$$K_{\text{in},2} = \frac{[\text{HgCl}^+][\text{Cl}^-]}{[\text{HgCl}_2]} = 10^{-7}, \quad [\text{HgCl}_2] \approx \text{conc. iniz.}$$

$$\text{Hg}^{+2} \approx 10^{-1} \text{ M}$$

$$[\text{HgCl}^+] = [\text{Cl}^-] =$$

$$K_{in,2} = \frac{[\text{HgCl}^+][\text{Cl}^-]}{[\text{HgCl}_2]} = \frac{[\text{Cl}^-]^2}{10^{-1}} = 10^{-7}$$

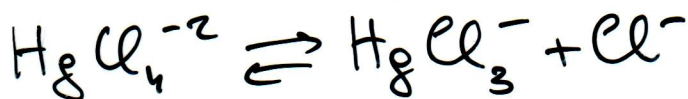
$$\underline{[\text{Cl}^-]} = \sqrt{10^{-8}} = \underline{10^{-4} \text{ M}} = \underline{[\text{HgCl}^+]}$$



$$K_{in,3} = \frac{[\text{HgCl}_2][\text{Cl}^-]}{[\text{HgCl}_3^-]} \approx 10^{-1} \quad [\text{Cl}^-] = [\text{HgCl}_2] = 10^{-4} \text{ M}$$

$$K_{in,3} = \frac{[\text{Cl}^-]^2}{[\text{HgCl}_3^-]} = \frac{(10^{-4})^2}{[\text{HgCl}_3^-]} = 10^{-1}$$

$$\underline{[\text{HgCl}_3^-]} = \underline{10^{-7} \text{ M}}$$



$$K_{in,4} = \frac{[\text{HgCl}_3^-][\text{Cl}^-]}{[\text{HgCl}_4^{-2}]} \approx 10^{-1}$$

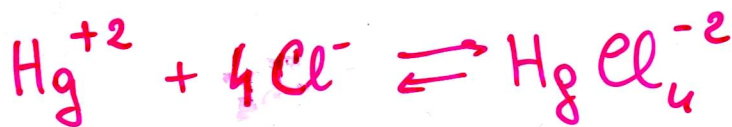
$$[\text{HgCl}_3^-] = [\text{Cl}^-] = 10^{-7} \text{ M}$$

$$K_{in,4} = \frac{[\text{HgCl}_3^-]^2}{[\text{HgCl}_4^{-2}]} = \frac{(10^{-7})^2}{[\text{HgCl}_4^{-2}]} = 10^{-1}$$

$$\underline{[\text{HgCl}_4^{-2}]} = \underline{10^{-13} \text{ M}}$$



$$K_{in,1} = \frac{[\text{Hg}^{+2}][\text{Cl}^-]}{[\text{HgCl}^+]} = 10^{-7} \quad ; \quad \underline{[\text{Hg}^{+2}]} = \underline{10^{-7} \text{ M}}$$



Situazione in forte eccesso di ligando



situazione con ligando stechiometrico

- In generale, quanto più grande è la conc. di ligando, tanto più piccola risulta la conc. del catione libero e tanto più grande risulta quella del complesso:



- Minore è la costante dielettrica del solvente, minore è il grado di dissociazione del complesso e quindi maggiore è la sua stabilità:



con aggiunta di

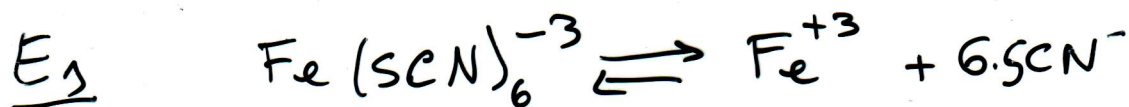
acetone, alcool, o

eter e

- Quando il complesso è molto stabile, non occorre aumentare la conc. di ligando (non c'è praticamente metallo libero):



- La diluizione aumenta la dissociaz. di un complesso.



inizio

c

-

-

eq.

c(1-α)

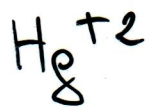
cα

cα

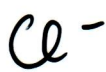
$$K_{in} = \frac{[\text{Fe}^{+3}][\text{SCN}^-]^6}{[\text{Fe}(\text{SCN})_6^{-3}]} = \frac{c\alpha \cdot (c\alpha)^6}{(1-\alpha) \cdot c} \approx c\alpha^7$$

3. CONTEMPORANEA PRESENZA DI DUE LIGANDI

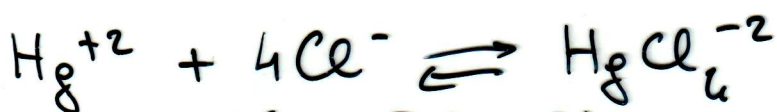
Es.



$$10^{-1} \text{ M}$$

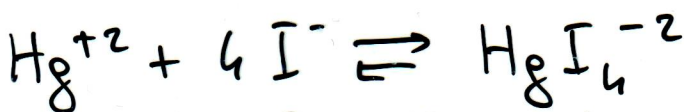


I^- entrambi alle conc. 1 M



$$K_{\text{intot}} = \frac{[\text{Hg}^{+2}][\text{Cl}^-]^4}{[\text{HgCl}_4^{-2}]} \approx 10^{-16}$$

$$\Delta\chi = 0.8$$



$$K_{\text{intot}} = \frac{[\text{Hg}^{+2}][\text{I}^-]^4}{[\text{HgI}_4^{-2}]} \approx 10^{-30}$$

$$\Delta\chi = 0.4$$

$$\frac{K_{\text{intot}}^{\text{HgCl}_4^{-2}}}{K_{\text{intot}}^{\text{HgI}_4^{-2}}} = \frac{10^{-16}}{10^{-30}} = \frac{[\text{Hg}^{+2}][\text{Cl}^-]^4 [\text{HgI}_4^{-2}]}{[\text{Hg}^{+2}][\text{I}^-]^4 [\text{HgCl}_4^{-2}]} = 10^{14}$$

$$K_{\text{intot}}^{\text{HgI}_4^{-2}} = \frac{[\text{Hg}^{+2}][\text{I}^-]^4}{[\text{HgI}_4^{-2}]} = 10^{-30} = \frac{[\text{Hg}^{+2}] \cdot 1}{10^{-1}}$$

poiché $[\text{HgI}_4^{-2}] = \text{conc. iniz. Hg}^{+2}$

$$[\text{Hg}^{+2}] = 10^{-31} \text{ M}$$

Nell'altro equilibrio: $K_{\text{intot}}^{\text{HgCl}_4^{-2}} = \frac{[\text{Hg}^{+2}] \cdot 1}{[\text{HgCl}_4^{-2}]} \approx 10^{-16}$

$$[\text{HgCl}_4^{-2}] = \frac{[\text{Hg}^{+2}]}{10^{-16}} = \frac{10^{-31}}{10^{-16}} = 10^{-15} \text{ M}$$