EQUILÍBRIO DE COMPLEXAÇÃO

Complexo é a entidade formada por um átomo ou íon metálico central, rodeada por espécies químicas, moléculas ou íons, denominadas ligantes

O conjunto constitui estrutura geométrica definida

Ligantes são espécies químicas, íons ou moléculas, apresentando pares de elétrons livres, não utilizados em ligações e portanto disponíveis

Admite-se que o ligante fornece pares de elétrons não compartilhados aos orbitais vazios do íon ou átomo metálico

$$Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}$$

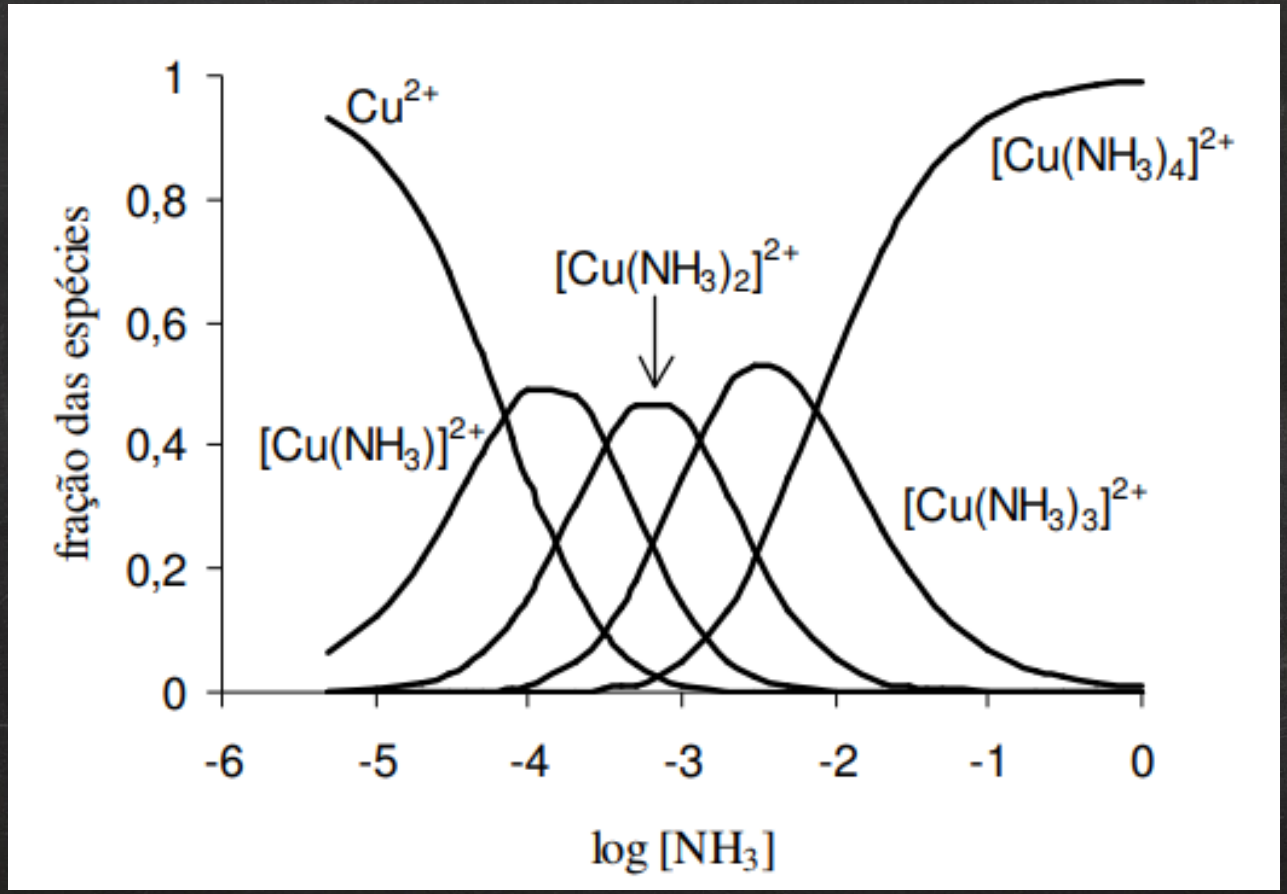
$$[Cu(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(H_2O)_3NH_3]^{2+} + H_2O \qquad K_{est\ 1}$$

$$[Cu(H_2O)_3NH_3]^{2+} + NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_2]^{2+} + H_2O \qquad K_{est\ 2}$$

$$[Cu(H_2O)_2(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(H_2O)(NH_3)_3]^{2+} + H_2O \qquad K_{est\ 3}$$

$$[Cu(H_2O)(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + H_2O \qquad K_{est\ 4}$$

$$[Cu(H_2O)_4]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O \qquad K_{est}$$

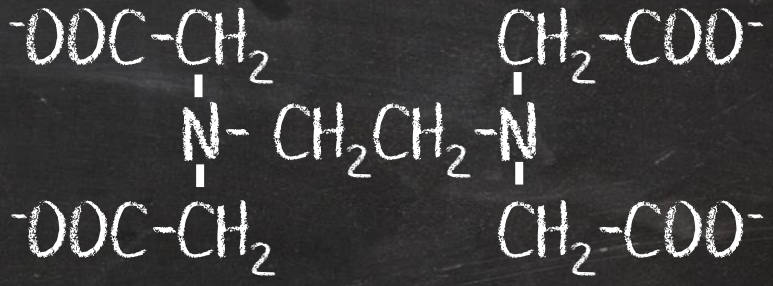

1
0,8
0,6
0,4
0,2
0
fração das espécies
Cu^{2+}
$[Cu(NH_3)_4]^{2+}$
$[Cu(NH_3)_2]^{2+}$
$[Cu(NH_3)]^{2+}$
$[Cu(NH_3)_3]^{2+}$
-6
-5
-4
-3
-2
-1
0
log $[NH_3]$

Ligantes Monodentados

Ligantes Polidentados

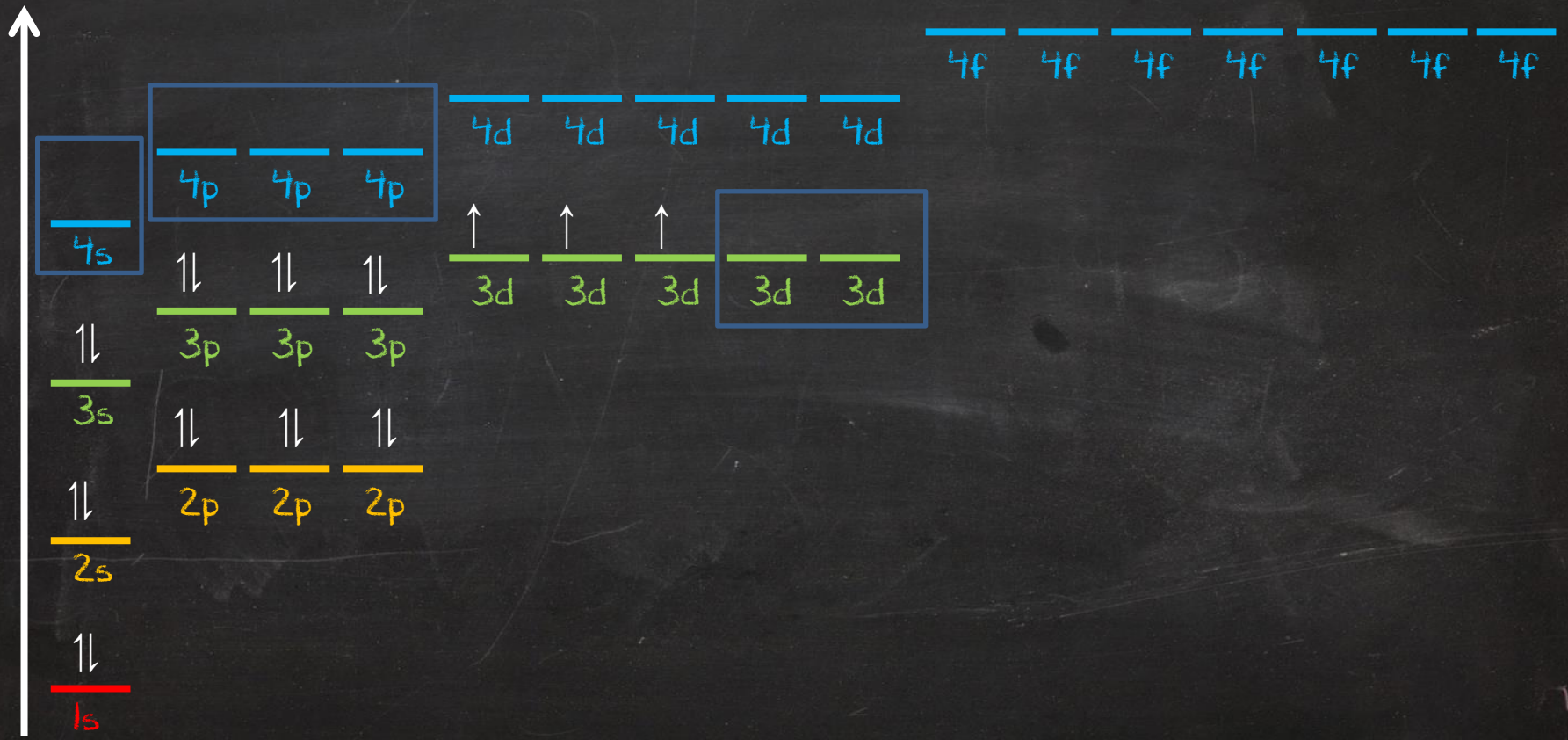
Etilenodiamina

Oxalato

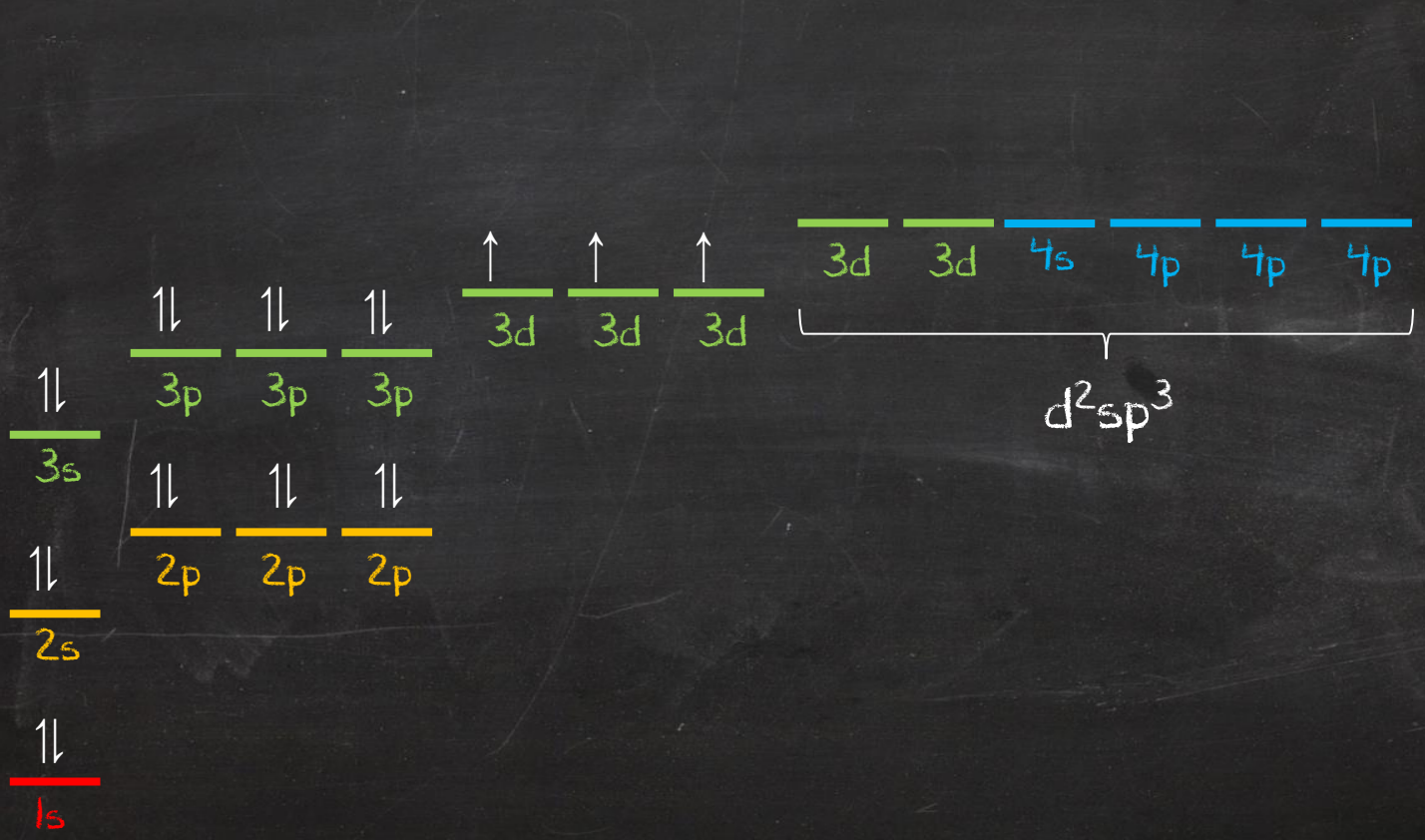


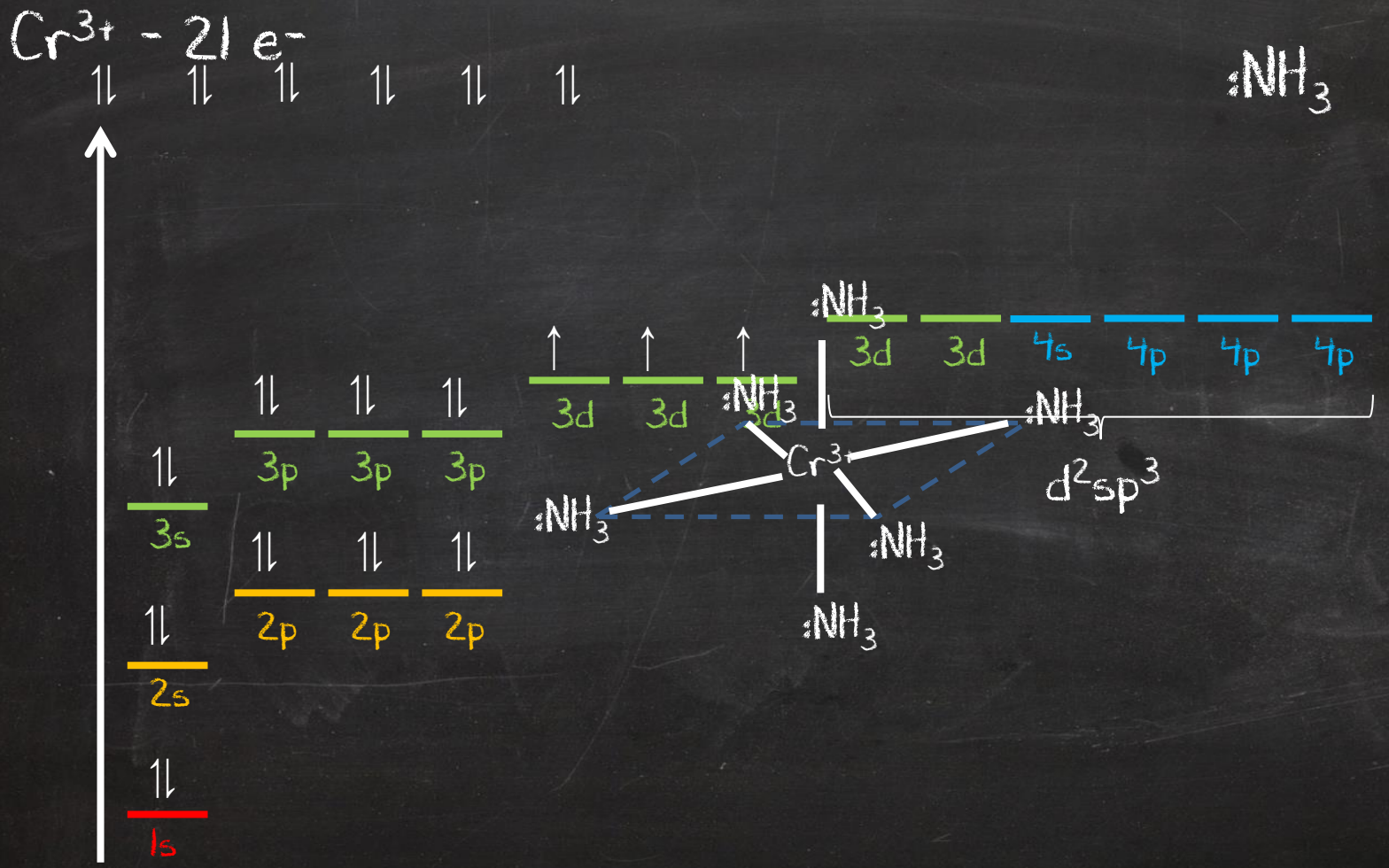
EDTA

Cr^{3+} - 21 e-


4f 4f 4f 4f 4f 4f 4f
4d 4d 4d 4d 4d
4p 4p 4p
4s
3d 3d 3d 3d 3d
3p 3p 3p
3s
2p 2p 2p
2s
1s

Cr^{3+} - 21 e-




Cr3+ - 21 e-
1s
2s
2p
3s
3p
3d
:NH3
d2sp3
4s
4p

Ni^{+2} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$ $4s^0\ 4p^0\ 4d^0$

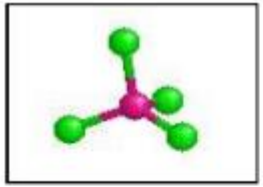
Ni^{+2} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ $3d^8$ $4s^0$ $4p^0$ $4d^0$

$[NiCl_4]^{-2}$, hibridização sp^3, estrutura tetraédrica, 4 ligantes Cl^-

$[Ni(CN)_4]^{-2}$, hibridização dsp^2, estrutura quadrado planar, 4 ligantes

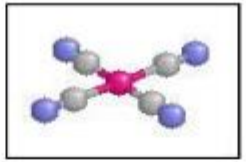
$[Ni(NH_3)_6]^{+3}$, hibridização d^2sp^3, estrutura octaédrica, 6 ligantes NH_3

$[Ag(NH_3)_2]^+$	Linear	$[MnCl_6]^{-3}$	Octaedro
$[Al(OH)_4]^-$	Tetraedro	$[NbF_7]^{-2}$	Bipiramide trigonal
$[AlF_6]^{-3}$	Octaedro	$[Ni(CN)_4]^{-2}$	Quadrado planar
$[Cd(CN)_4]^{-2}$	Tetraedro	$[Ni(CO)_4]$	Tetraedro
$[CoCl_4]^{-2}$	Tetraedro	$[Ni(en)_2Cl_2]$	Octaedro
$[Cr(CN)_6]^{-4}$	Octaedro	$[Ni(NH_3)_6]^{+2}$	Octaedro
$[Cr(NH_3)_6]^{+3}$	Octaedro	$[Ni(ox)_2]$	Quadrado planar
$[Cu(CN)_2]^-$	Linear	$[Pt(NH_3)_4]^{+2}$	Quadrado planar
$[Cu(NH_3)_4]^{+2}$	Quadrado planar	$[MnCl_6]^{-3}$	Octaedro
$[Fe(CN)_6]^{-4}$	Octaedro	$[PtCl_4]^{-2}$	Tetraedro
$[Fe(CO_5)]$		$[PtCl_6]^{-2}$	octaedro
$[Fe(ox)_3]^{-3}$	Octaedro	$[Zn(CN)_4]^{-2}$	Tetraedro
$[Fe(SCN)_6]^{-3}$	Octaedro	$[Zn(NH_3)_4]^{+2}$	Tetraedro
$[FeCl_4]^-$	Tetraedro	$[Zn(OH)_4]^{-2}$	Tetraedro
$[HgCl_3]^-$	Trigonal planar	$[PtCl_4]^{-2}$	Tetraedro

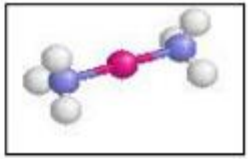


$[CoCl_4]^{-2}$

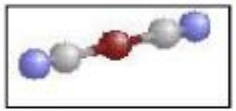
$[PtCl_6]^{-2}$



$[Ni(CN)_4]^{-2}$

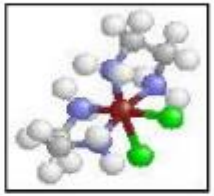


$[Ag(NH_3)_2]^{+}$

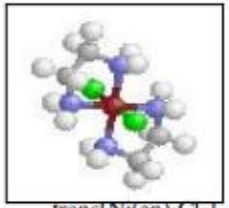


$[Cu(NH_3)]^{+}$

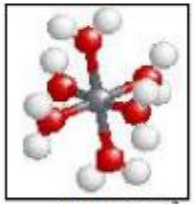
$[HgS_2]^{-2}$



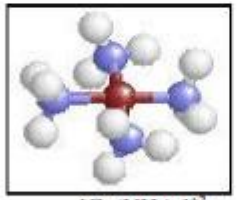
$cis[Ni(en)_2Cl_2]$



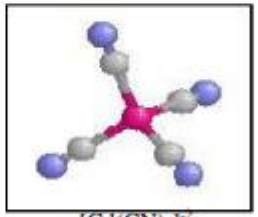
$trans[Ni(en)_2Cl_2]$



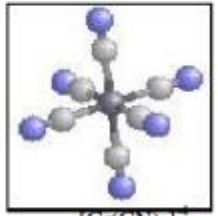
$[Ni(H_2O)_6]^{+2}$



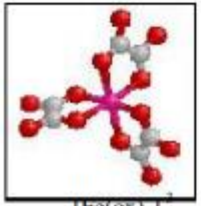
$[Cu(NH_3)_4]^{+2}$



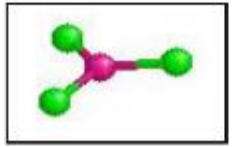
$[Cd(CN)_4]^{-2}$



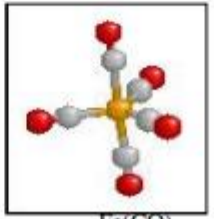
$[Cr(CN)_6]^{-3}$



$[Fe(ox)_3]^{-3}$



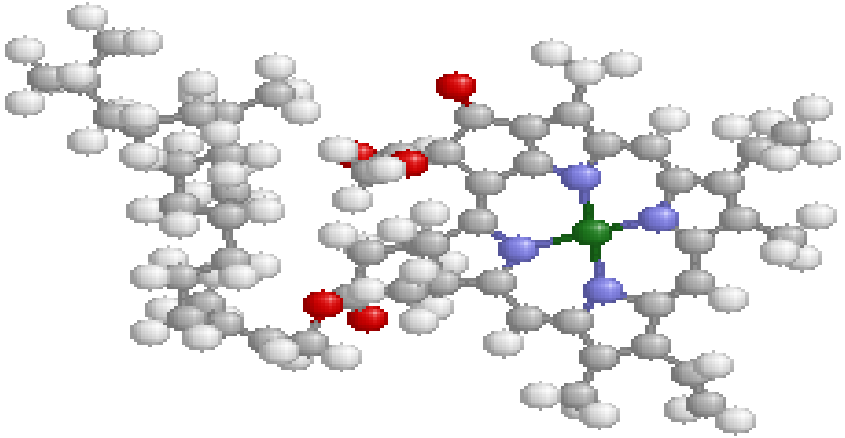
$[HgCl_3]^{-}$



$Fe(CO)_5$

$[NbF_7]^{-2}$

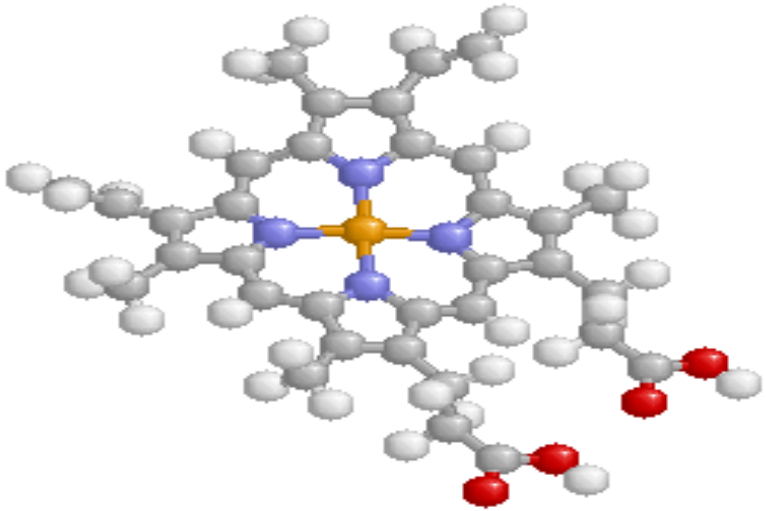
CLOROFILA A



Nitrogênio
Magnésio
Oxigênio
Carbono
Hidrogênio

Um dos pigmentos verdes das plantas, a Clorofila A absorve luz vermelha e púrpura e luz verde é refletida. Note-se a estrutura quadrado planar em volta do magnésio.

HEME



Nitrogênio

Ferro

Oxigênio

Carbono

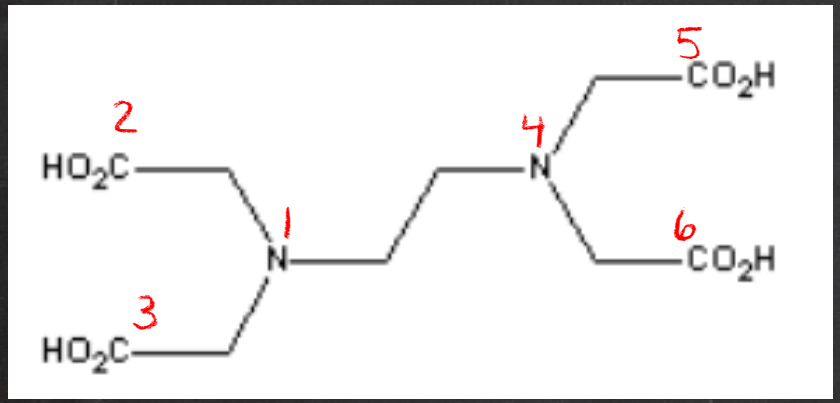
Hidrogênio

Constante de estabilidade

$$[M(H_2O)_6]^{n+} + mL \rightleftharpoons [ML_m] + 6H_2O$$

$$Kest = \frac{[ML_m]}{[M(H_2O)_6]^{n+}\,[mL]}$$

EDTA - Ácido Etileno Diamino Tetra-acético

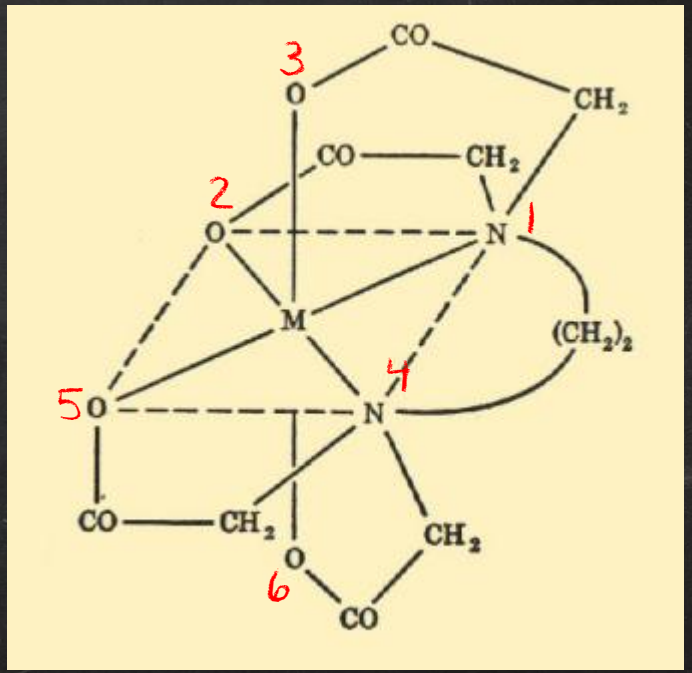


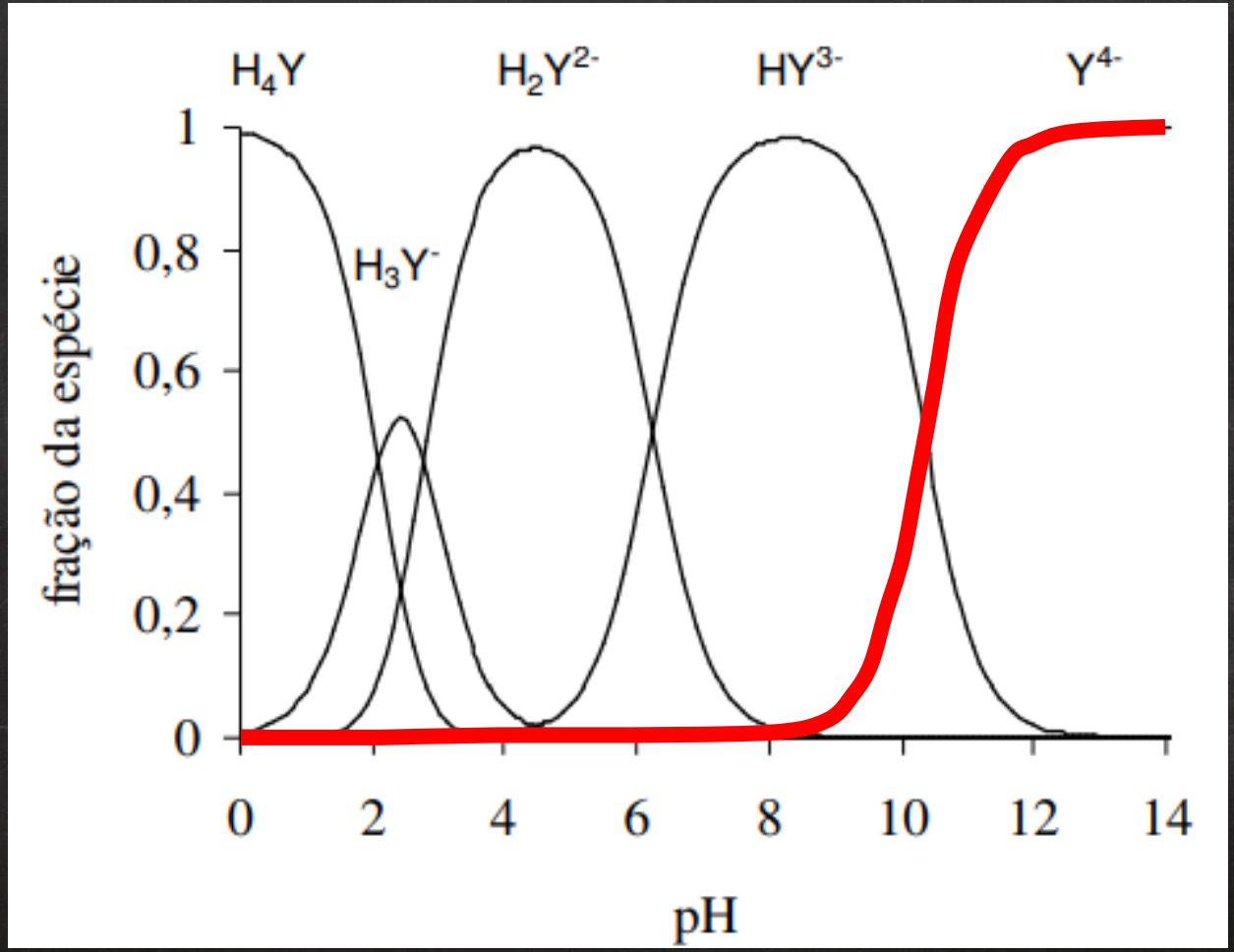
$$H_4Y \rightleftharpoons H_3Y^- + H^+$$

$$H_3Y^- \rightleftharpoons H_2Y^{2-} + H^+$$

$$H_2Y^{2-} \rightleftharpoons HY^{3-} + H^+$$

$$HY^{3-} \rightleftharpoons Y^{4-} + H^+$$




H_4Y
H_2Y^{2-}
HY^{3-}
Y^{4-}
H_3Y^-
1
0,8
0,6
0,4
0,2
0
fração da espécie
0
2
4
6
8
10
12
14
pH

pH	Fração de Y^{4-}	pH	Fração de Y^{4-}
1	3,6637E-18	8	0,00447
2	1,9880E-14	9	0,04363
3	1,6147E-11	10	0,31366
4	2,4752E-09	11	0,82049
5	2,4740E-07	12	0,97859
6	1,6689E-05	13	0,99781
7	0,00039	14	0,99978

Ión metálico	log K_{est}	Ión metálico	log K_{est}
Fe^{3+}	25,1	Al^{3+}	16,13
Th^{2+}	23,2	La^{3+}	15,50
Hg^{2+}	21,8	Fe^{2+}	14,33
Cu^{2+}	18,8	Mn^{2+}	13,79
Ni^{2+}	18,62	Ca^{2+}	10,70
Pb^{2+}	18,04	Mg^{2+}	8,69
Zn^{2+}	16,50	Sr^{2+}	8,63
Cd^{2+}	16,46	Ba^{2+}	7,76
Co^{2+}	16,31	Ag^{2+}	7,3

Exemplo: Em uma solução de Ca^{2+} com concentração 0,1 mol L^{-1}, EDTA 0,2 mol L^{-1} e pH 2, qual será a porcentagem de cálcio complexado? $K_{est} = 5,01 \times 10^{10}$; $\alpha_{pH=2} = 1,99 \times 10^{-14}$

$$Ca^{2+} + Y^{4-} \rightleftharpoons [CaY]^{2-}$$

$$Kest = \frac{[CaY]^{2-}}{[Ca^{2+}]\,[Y^{4-}]}$$

$[Y^{4-}]$ ➡ EDTA x α_{pH2}

$0,2 \times 1,99 \times 10^{-14} = 3,98 \times 10^{-15}$

$$5,01 \times 10^{10} = \frac{X}{(0,1-x)\ 3,98 \times 10^{-15}}$$

$$5{,}01\times10^{10} = \frac{X}{(0{,}1-x)\ 3{,}98\times10^{-15}}$$

$$5{,}01\times10^{10} = \frac{X}{3{,}98\times10^{-16} - 3{,}98\times10^{-15}X}$$

$$1{,}99\times10^{-5} - 1{,}99\times10^{-4}X = X$$

$X = 1{,}99\times10^{-5}$

$0{,}1$ ----- 100%

$1{,}99\times10^{-5}$ ----- ?

$0{,}0199 \sim 0{,}02\%$