Química Bioinorgánica

Introducción General

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Curso de Introducción a la Química Bioinorgánica.
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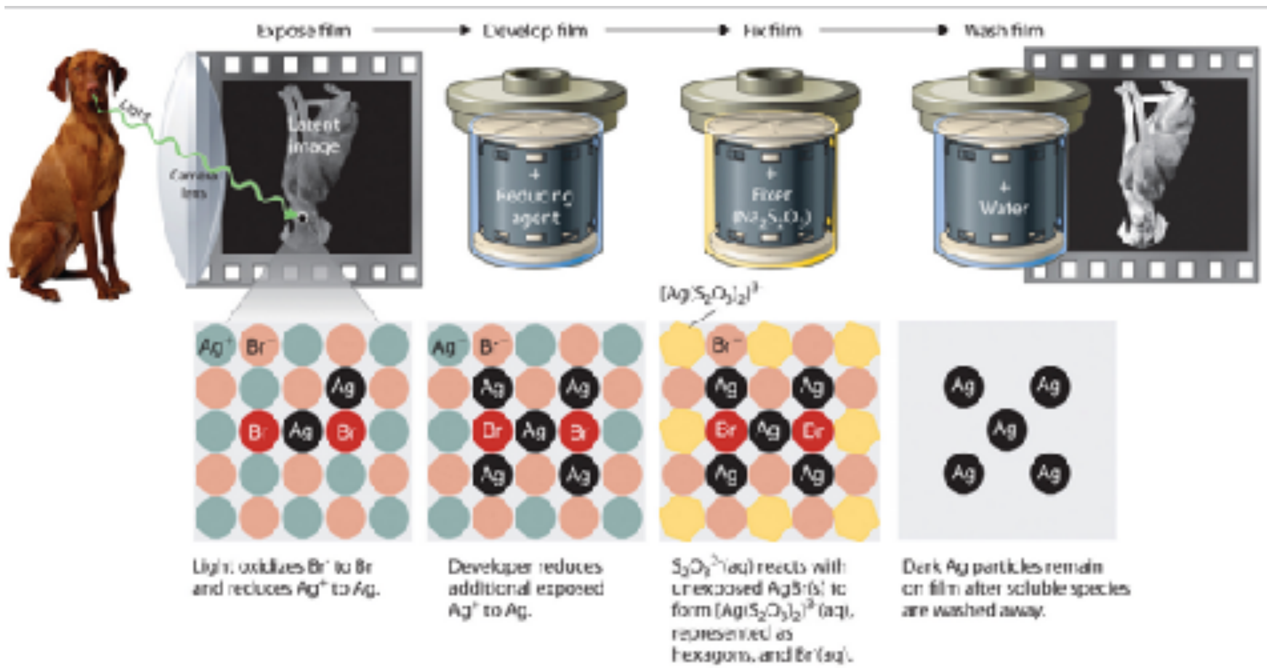
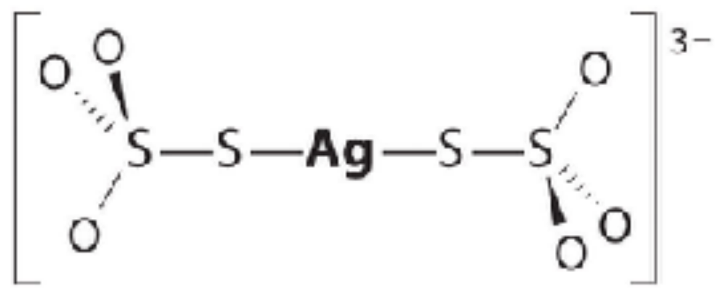
Universidad de Santiago de Chile

Estabilidad de iones complejos: Importancia

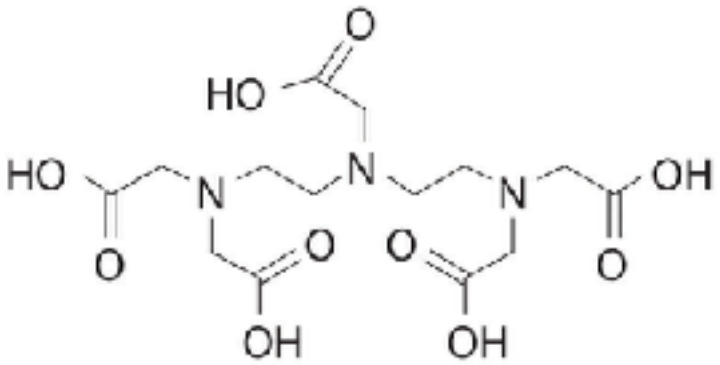


AgBr + $S_20_3^{-2}$

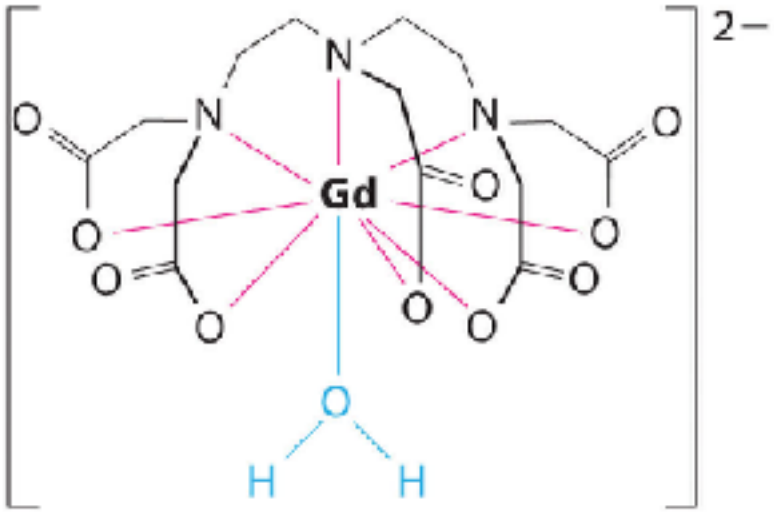


thiosulfate complex of Ag$^+$

Estabilidad de iones complejos: Importancia

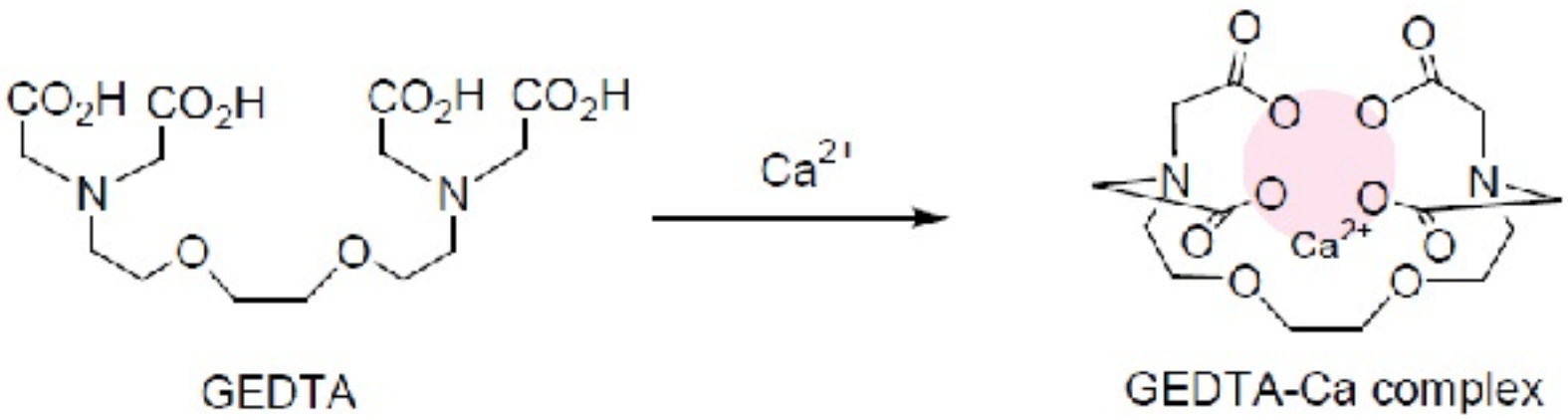


DTPA (diethylenetriaminepentaacetic acid)

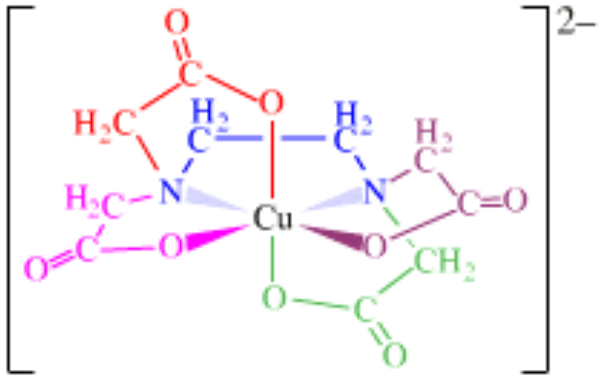


gadolinium-DTPA complex,
$[Gd(DTPA{\cdot}H_2O)]^{2-}$

Estabilidad de iones complejos: Importancia



Ca^{+2} + $EDTA^{-4}$ ------> $CaEDTA^{-2}$



Estabilidad de iones complejos

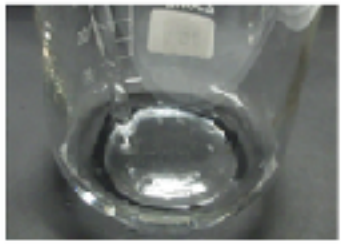
$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

$$K_a = \frac{[CN^-] \cdot [H_3O^+]}{[HCN]}$$

$$K_f = \frac{\left[[Cu(NH_3)_4]^{2+}\right]}{[Cu^{2+}][NH_3]^4} = 2.1 \times 10^{13}$$

Constantes de estabilidad

+ Ag^+

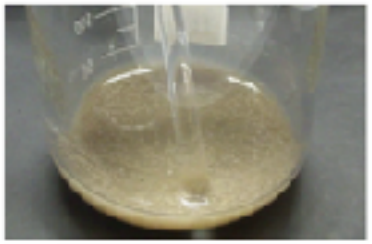


$AgNO_3$ solution

+ CO_3^{-2}

Step 1 (Ag_2CO_3)

+ NaOH



Step 2 (AgOH)

+ NaCl

Step 3 (AgCl)

Step 4: $Ag(NH_3)_2^+$

+ NH_3

Step 5: AgI

+ KI

Factores que determinan K_f:

$$M + L \leftrightarrows ML + \Delta$$

$$K_1 = \frac{[ML]}{[M][L]}$$

La constante de estabilidad mide la cantidad de calor desprendida y la variación de **entropía** o desorden.

Factores que determinan Kf: Efecto iónico

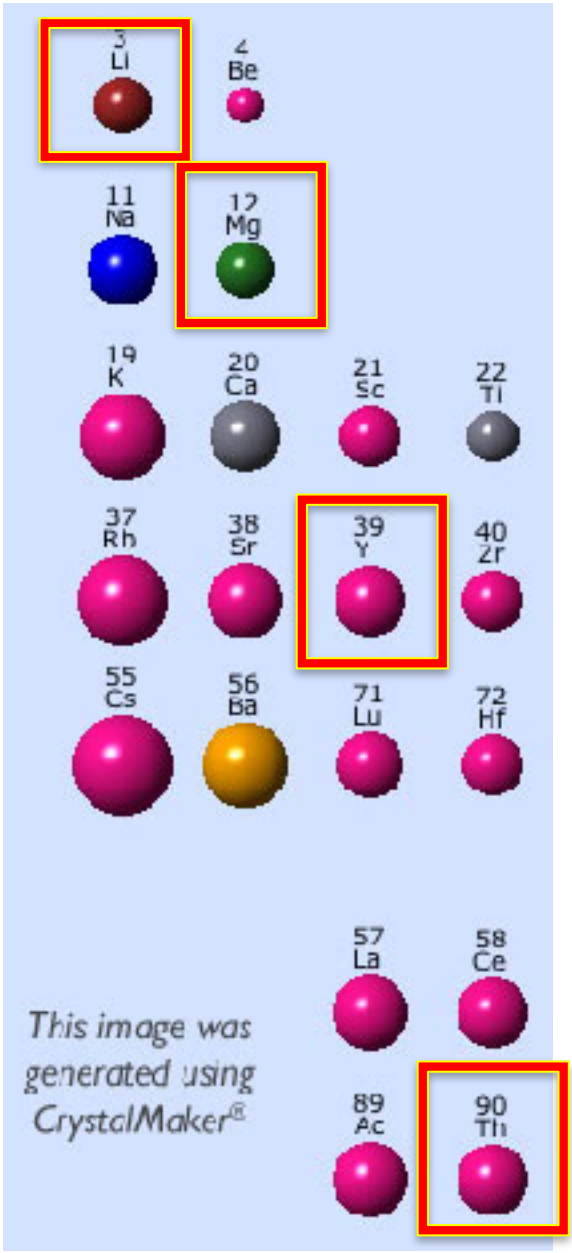
Aumento de carga

$K_{LiOH} = 2$

$K_{MgOH}^{+} = 100$

$K_{YOH}^{+2} = 10^{7}$

$K_{ThOH}^{+3} = 10^{10}$



Iron $^{2+}$

Iron $^{3+}$

Factores que determinan Kf: Efecto iónico

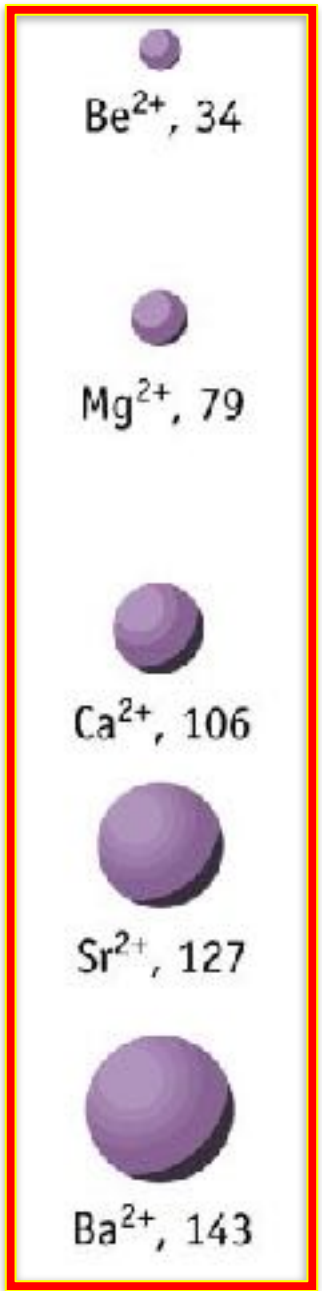
Aumento del radio iónico

$K_{BeOH}^{+} = 10^{7}$

$K_{MgOH}^{+} = 120$

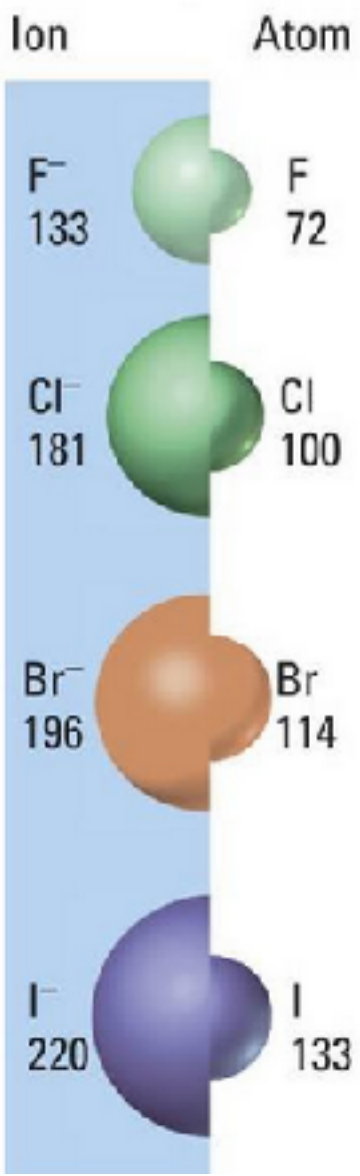
$K_{CaOH}^{+} = 30$

$K_{BaOH}^{+} = 4$



$K_{YOH}^{+2} = 10^{7}$

Factores que determinan K_f: Efecto iónico



$K_{FeF}^{+2} = 1X10^{6}$

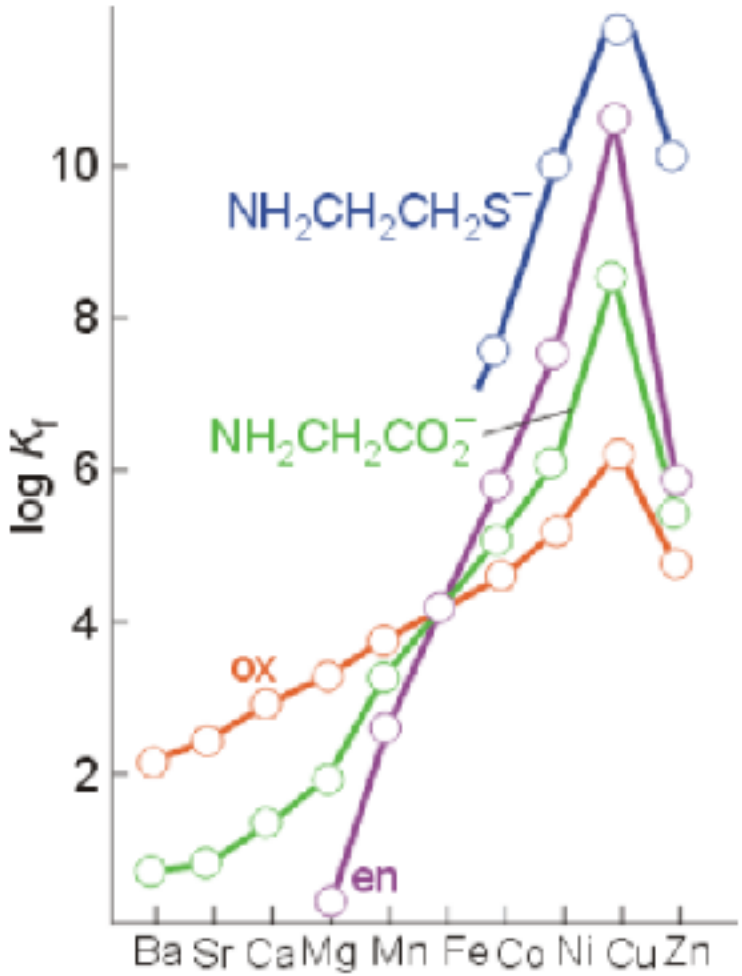
$K_{FeCl}^{+2} = 2x10^{1}$

ClO_4^-

K_f = ???

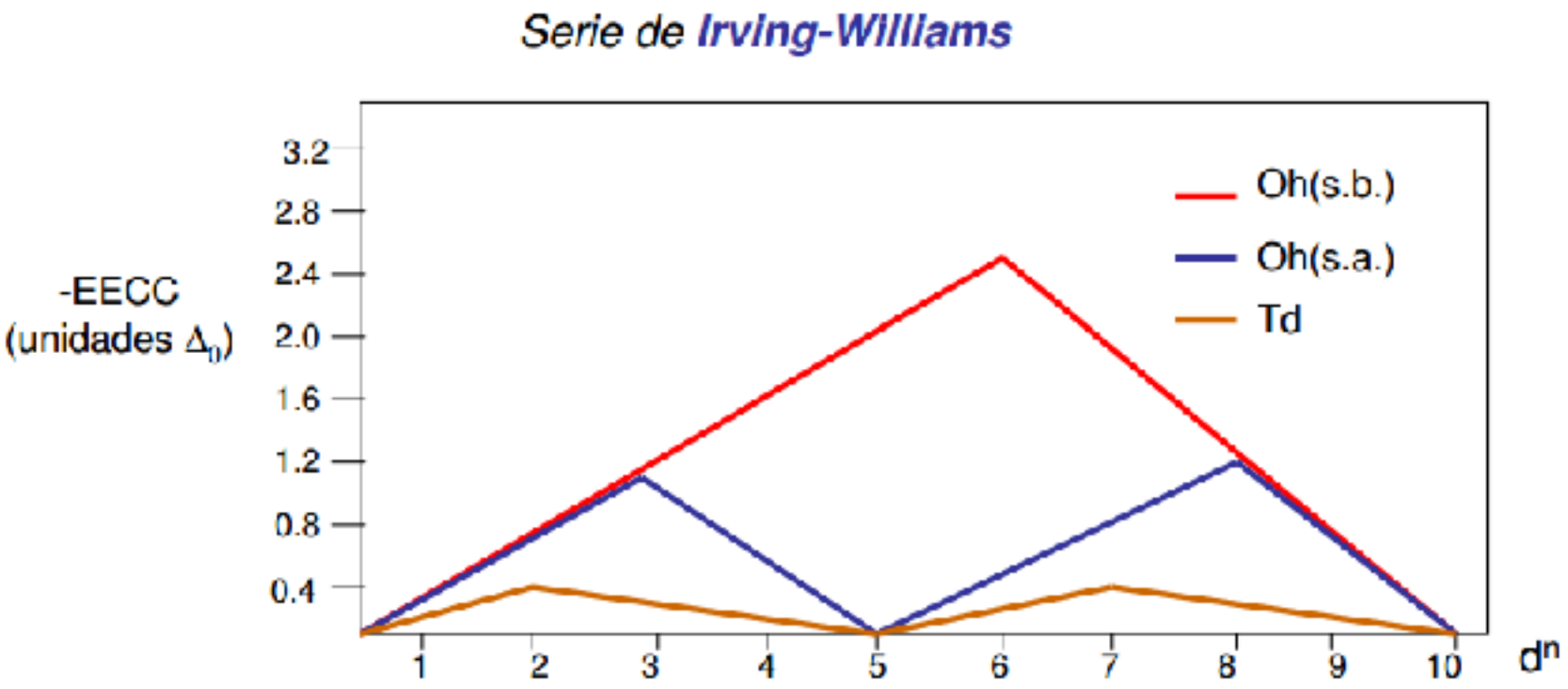
Factores que determinan Kf: E.E.C.C.

$$[M(H_2O)_6]^{2+} + 6X^- \leftrightarrows [MX_6]^{4-} + 6H_2O(l)$$

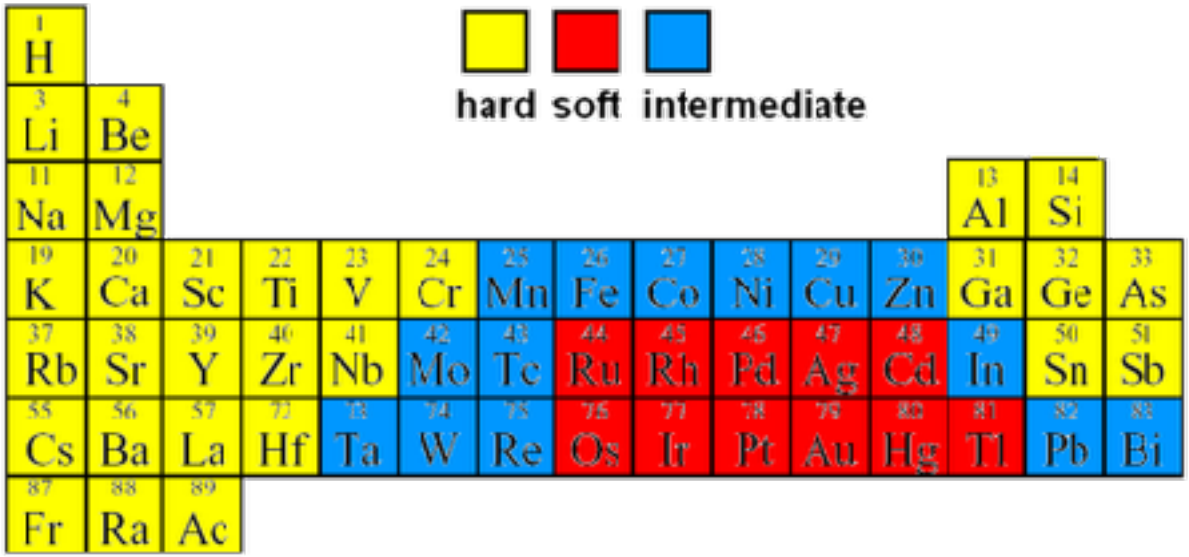


Factores que determinan Kf: EECC

$$[M(H_2O)_6]^{2+} + 6X^- \leftrightarrows [MX_6]^{4-} + 6H_2O(l)$$



Ácidos y bases: duros y blandos



Dureza
O>N

Pt, Au, Hg y Pb

H_20 vs NH_3

Ti, V y Cr

Ácidos y bases: duros y blandos

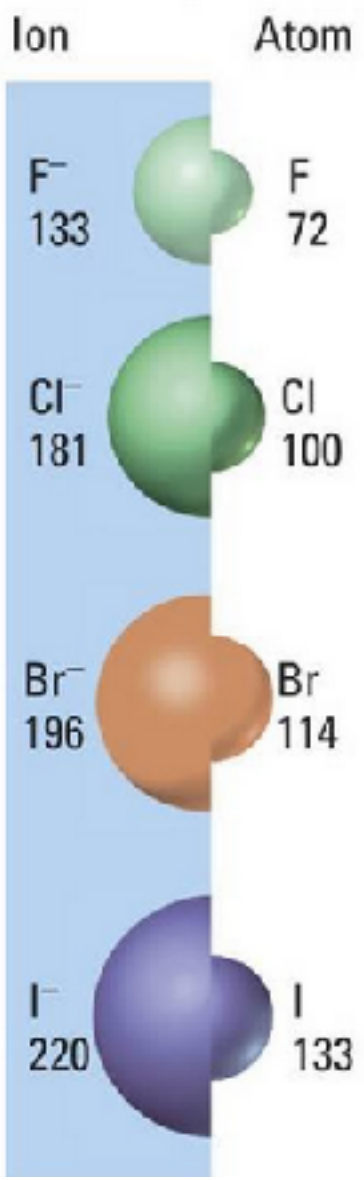
Formation Constants of Selected Complex Ions in Water at 25°C

Complex Ion	Equilibrium Expression	Formation Constant (K_f)
$Ag(NH_3)_2^+$	$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$	1.5×10^7
$Ag(CN)_2^-$	$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$	1.0×10^{21}
$Cu(CN)_4^{2-}$	$Cu^{2+} + 4CN^- \rightleftharpoons Cu(CN)_4^{2-}$	1.0×10^{25}
$Cu(NH_3)_4^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$	5.0×10^{13}
$Cd(CN)_4^{2-}$	$Cd^{2+} + 4CN^- \rightleftharpoons Cd(CN)_4^{2-}$	7.1×10^{16}
CdI_4^{2-}	$Cd^{2+} + 4I^- \rightleftharpoons CdI_4^{2-}$	2.0×10^6
$HgCl_4^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-}$	1.7×10^{16}
HgI_4^{2-}	$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	2.0×10^{30}
$Hg(CN)_4^{2-}$	$Hg^{2+} + 4CN^- \rightleftharpoons Hg(CN)_4^{2-}$	2.5×10^{41}
$Co(NH_3)_6^{3+}$	$Co^{3+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$	5.0×10^{31}
$Zn(NH_3)_4^{2+}$	$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$	2.9×10^9

Base blando: CN-, I-,
Base duras: NH_3, Cl^-, F^-

Ácidos blandos: Hg, Ag

Ácidos y bases: duros y blandos



$Ag^+ + X^- \leftrightarrows AgX$

$K_{AgF} = 2$

$K_{AgCl} = 2X10^3$

$K_{AgBr} = 3X10^4$

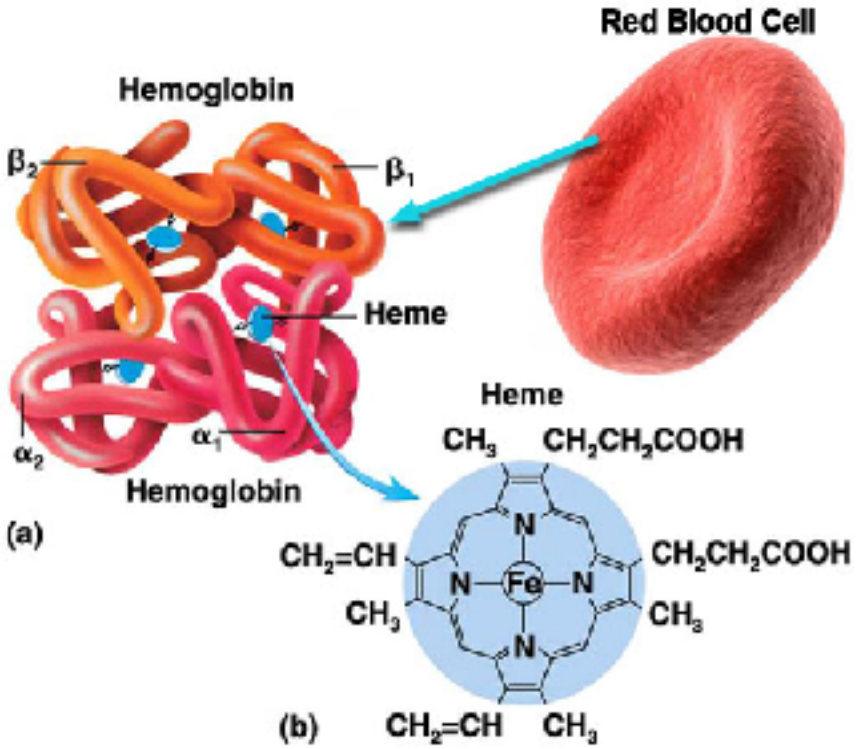
$K_{AgI} = 1X10^8$

¿Enlace covalente?
¿S?

Ácidos: blandos

$Fe^{2+} + 6CN^- \text{ ----- } [Fe(CN)_6]^{4-}$ $K = 1.8 \times 10^6$

$Fe^{3+} + 6CN^- \text{ ----- } [Fe(CN)_6]^{3-}$ $K = 1.2 \times 10^{31}$

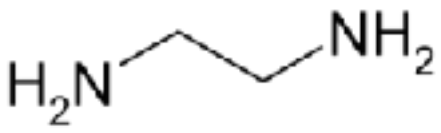


Efecto quelato

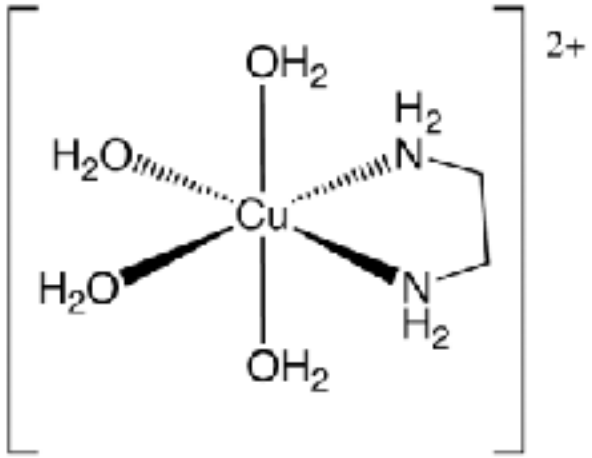
$$M(OH_2)_2^{2+} + en \rightleftharpoons M(en)^{2+} + 2H_2O$$

$$M(OH_2)_2^{2+} + 2NH_3 \rightleftharpoons M(NH_3)_2^{2+} + 2H_2O$$

Cu^{+2}: $\log K_1 = 10.6$ $\log \beta_2 = 7.7$

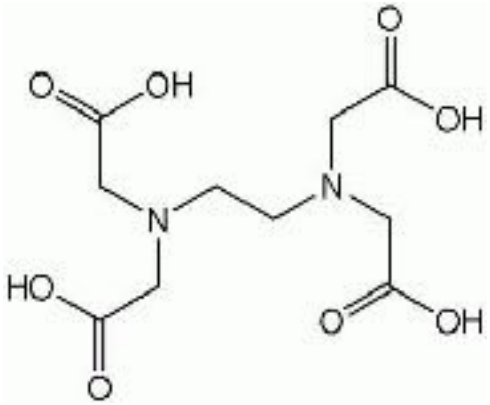


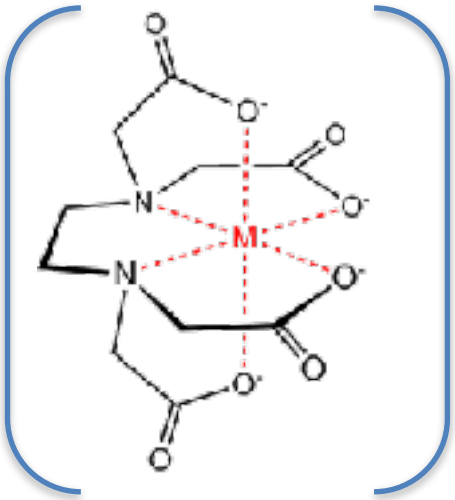
Cu^{+2}



Efecto quelato

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





-2

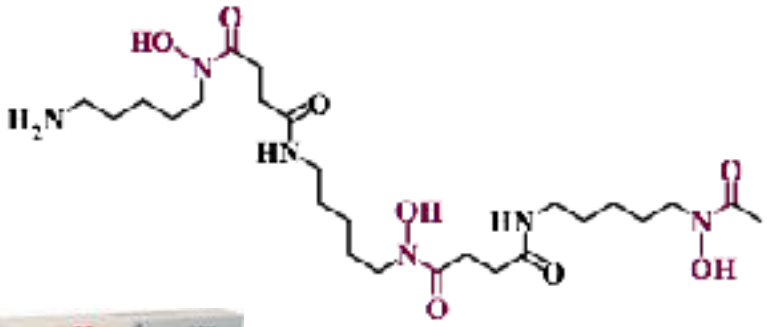
+ $6H_2O$

$K_{Ni(NH_3)_6^{+2}} = 1X10^8$

$K_{NiEDTA^{-2}} = 4,2X10^{18}$

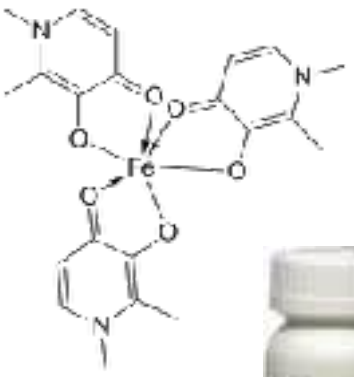
Importancia de la estabilidad de los complejos metálicos

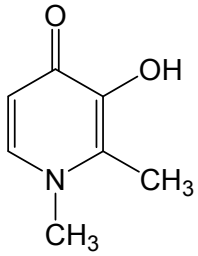
Terapias de quelación



Desferrioxamina (sideroforo natural)

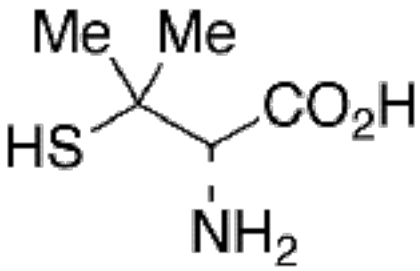
Kf = 10^{31}





Deferiprona

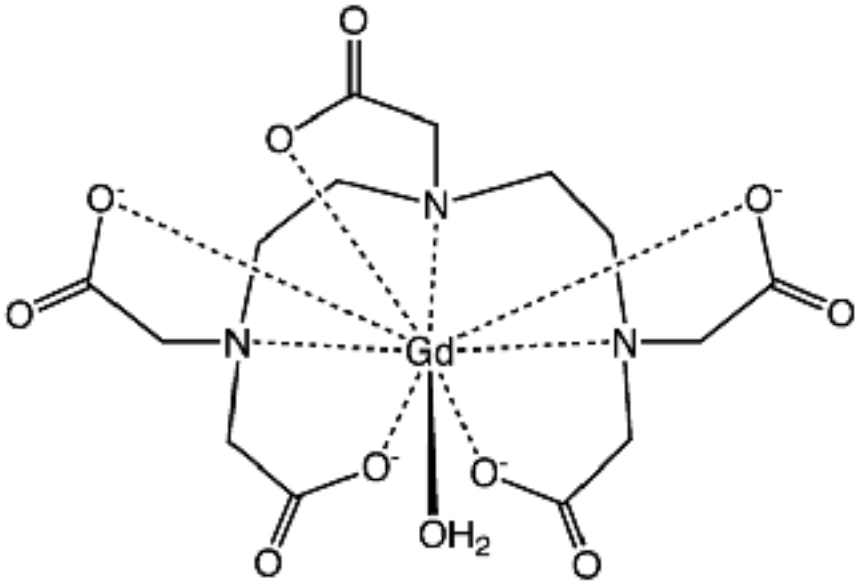
Cuprimina®



Remueve Cu que provoca mal de Wilson

Importancia de la estabilidad de los complejos metálicos

DTPA: agente de contraste paramagnético utilizado para estudios por resonancia magnética.

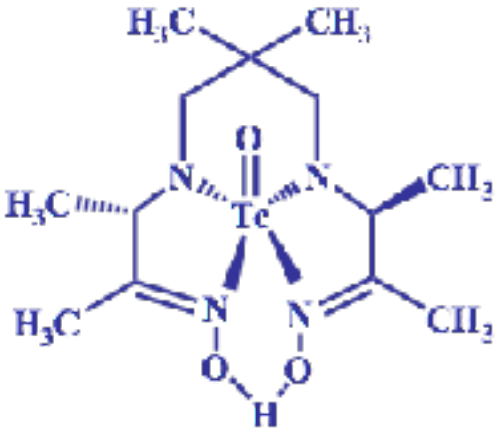


GaDTPA: $K=1X10^{22}$

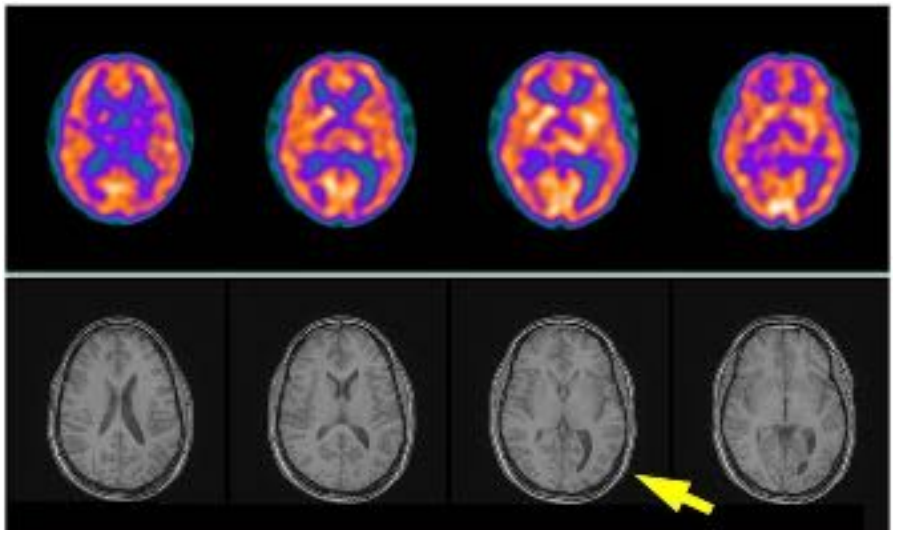
GaEDTA: $K= 1X10^{17}$

Importancia de la estabilidad de los complejos metálicos

SPECT imaging: intravenous injection of the γ isotope 99mTc complex for detection of altered regional cerebral perfusion (imaging actual brain function) (Alzheimer's disease)



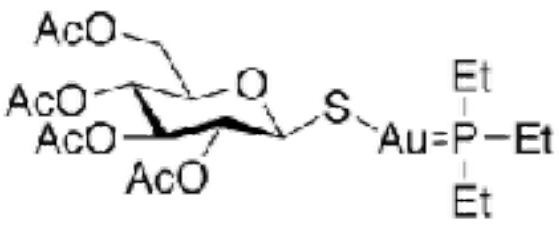
99mTc(γ)
$t_{1/2}$ = 6.03 h

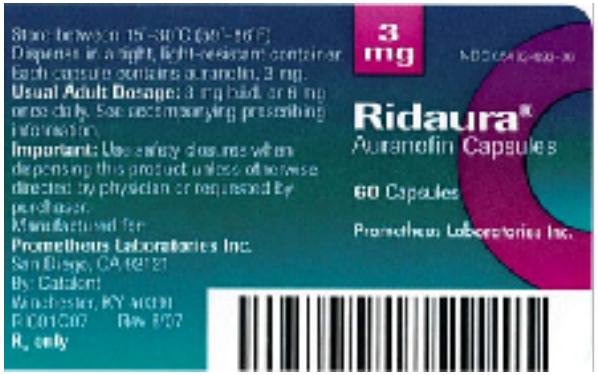


Importancia de la estabilidad de los complejos metálicos

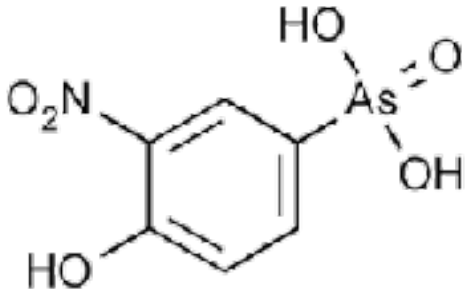
Auranofin

Anti-arthritic agent





Roxarsone



Aumentar la ganancia de peso y mejorar la eficiencia de la alimentación, y como un coccidiostático (agente antiprotozoario que actúa sobre parásitos coccidios)

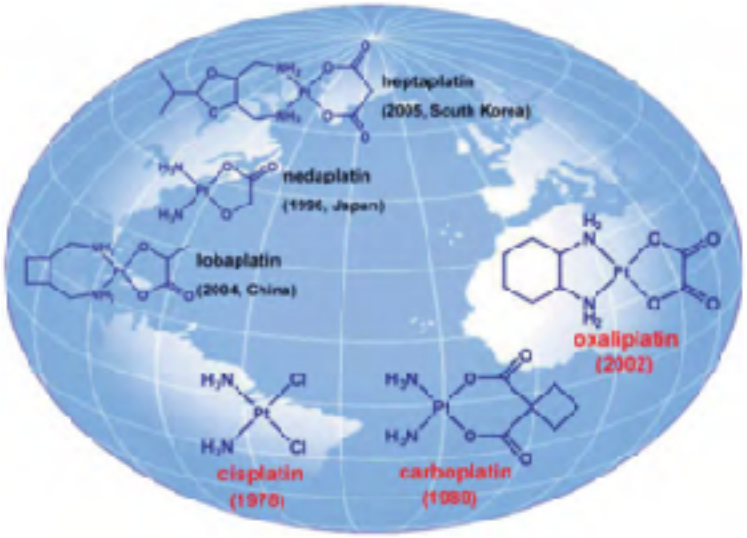
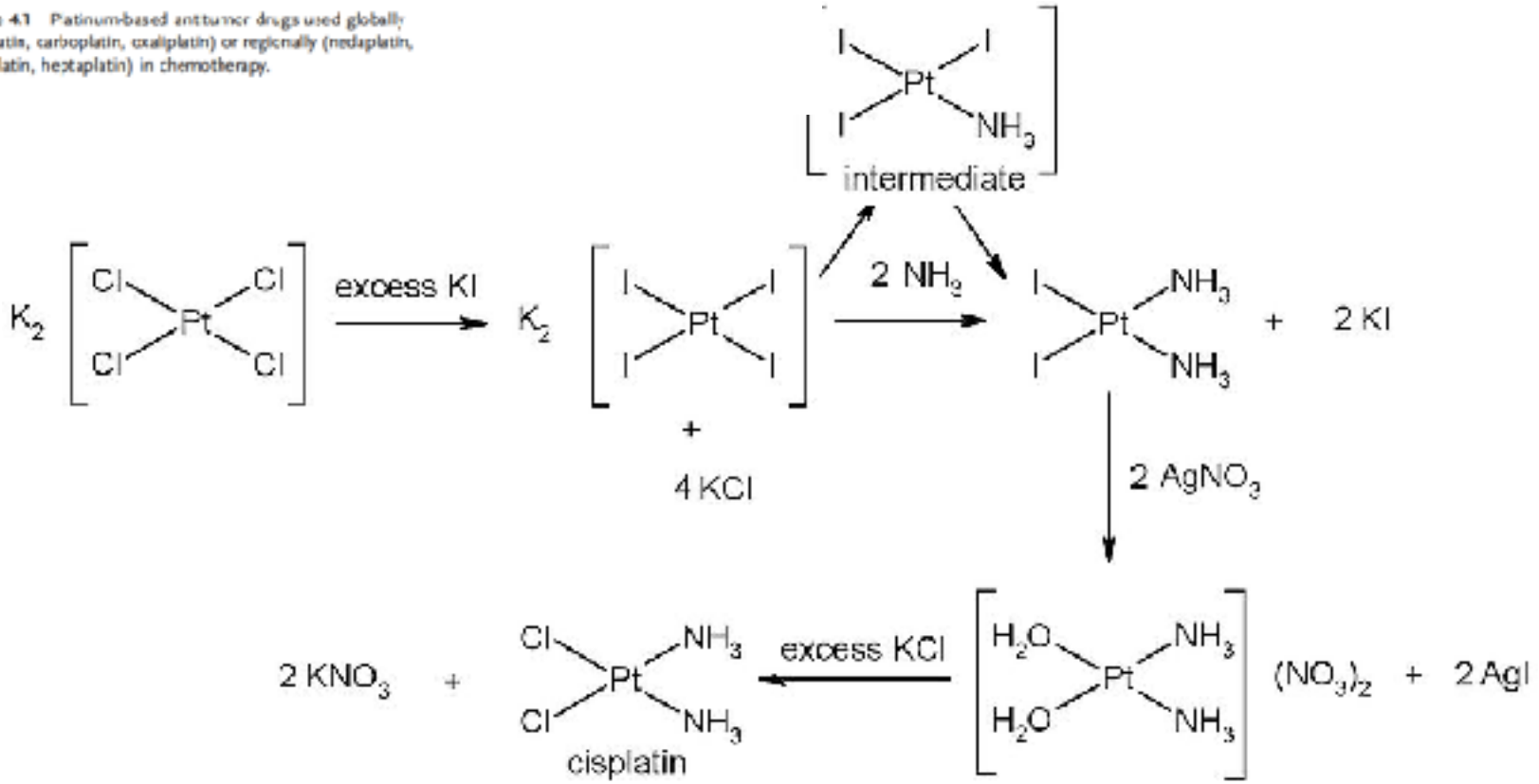


Figure 4.1 Platinum-based antitumor drugs used globally (cisplatin, carboplatin, oxaliplatin) or regionally (nedaplatin, lobaplatin, heptaplatin) in chemotherapy.



Fin de la clase…