Coordination equilibria

Stability and competition

$M^{n+} + :L \leftrightarrow M:L^{n+}$

Wilson's disease

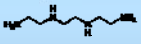
A recessive genetic disorder resulting in copper accumulation in liver and brain:

Liver problems and
neurological and psychiatric symptoms

Treatment: chelation therapy

Chelation therapy

To decrease copper levels in liver:
penicillamine (orally) 

or triethylenetetramine 

Why these ligands?
What about zinc-levels?

Selectivity ? (relies on relative stabilities)

Competition

Many metal ions and many ligands in one solution:

Competition between M_1 and M_2 and H^+ for L_1
and
Competition between L_1 and L_2 for M_1

Selectivity ?

One metal ion wanted M_1 – One ligand L_1 used.

Still: Many metal ions and many ligands in one solution:
Competition between M_1 and M_2 and H^+ for L_1
Competition between L_1 and L_2 for M_1

Selectivity is affected (capture of M_1 by L_1) by:
High $[M_1L_1]$ and $[M_2L_2]$/ $[HL_2^+]$ to decrease:
$[M_1L_2]$ and $[M_2L_1]$/ $[HL_1^+]$ (low)

Selective capture

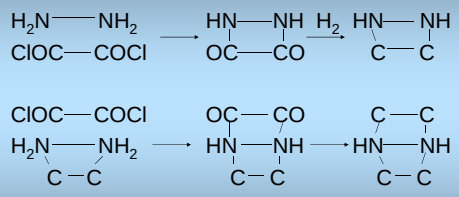
$$[M_1L_1] = [M_1]\cdot[L_1]\cdot K_{11}$$

$[M_1L_2] = [M_1]\cdot[L_2]\cdot K_{12}$ ($K_{12} < K_{11}$)
$[M_2L_1] = [M_2]\cdot[L_1]\cdot K_{21}$ ($K_{21} < K_{11}$)
$[HL_1^+] = [H^+]\cdot[L_1]\cdot 10^{pK_1}$ (L_1 not too basic)

Selective uptake

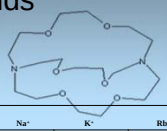
uptake	Na^+,K^+	Mg^{2+},Ca^{2+}	Zn^{2+},Cu^{2+}	ligand
[M]	10^{-1}	10^{-3}	10^{-7}	
K_{ML}	> 10	< 10^2	< 10^6	O-macro-
$[M]\cdot K_{ML}$	> 1	< 0.1	< 0.1	cycles
K_{ML}	1	> 10^3	< 10^6	Di/tri car-
$[M]\cdot K_{ML}$	< 0.1	> 1	< 0.1	boxylates
K_{ML}	0.1	< 10^2	< 10^7	N-or S-
$[M]\cdot K_{ML}$	< 0.1	< 0.1	> 1	ligands

Cryptands



Na^+, K^+ ligand: Cryptands

Cryptand [2,2,2]



O's in chains	Hole size/Å	LogK Li^+	Na^+	K^+	Rb^+
2,1,1	1.6	5.3	2.8	<2	<2
2,2,1	2.2	2.5	5.4	3.9	2.55
2,2,2	2.8	<2	3.9	5.4	4.35
3,2,2	3.6	2	1.65	2.2	2.05
3,3,2	4.2	<2	<2	<2	<0.7
3,3,3	4.8	<2	<2	<2	<0.5