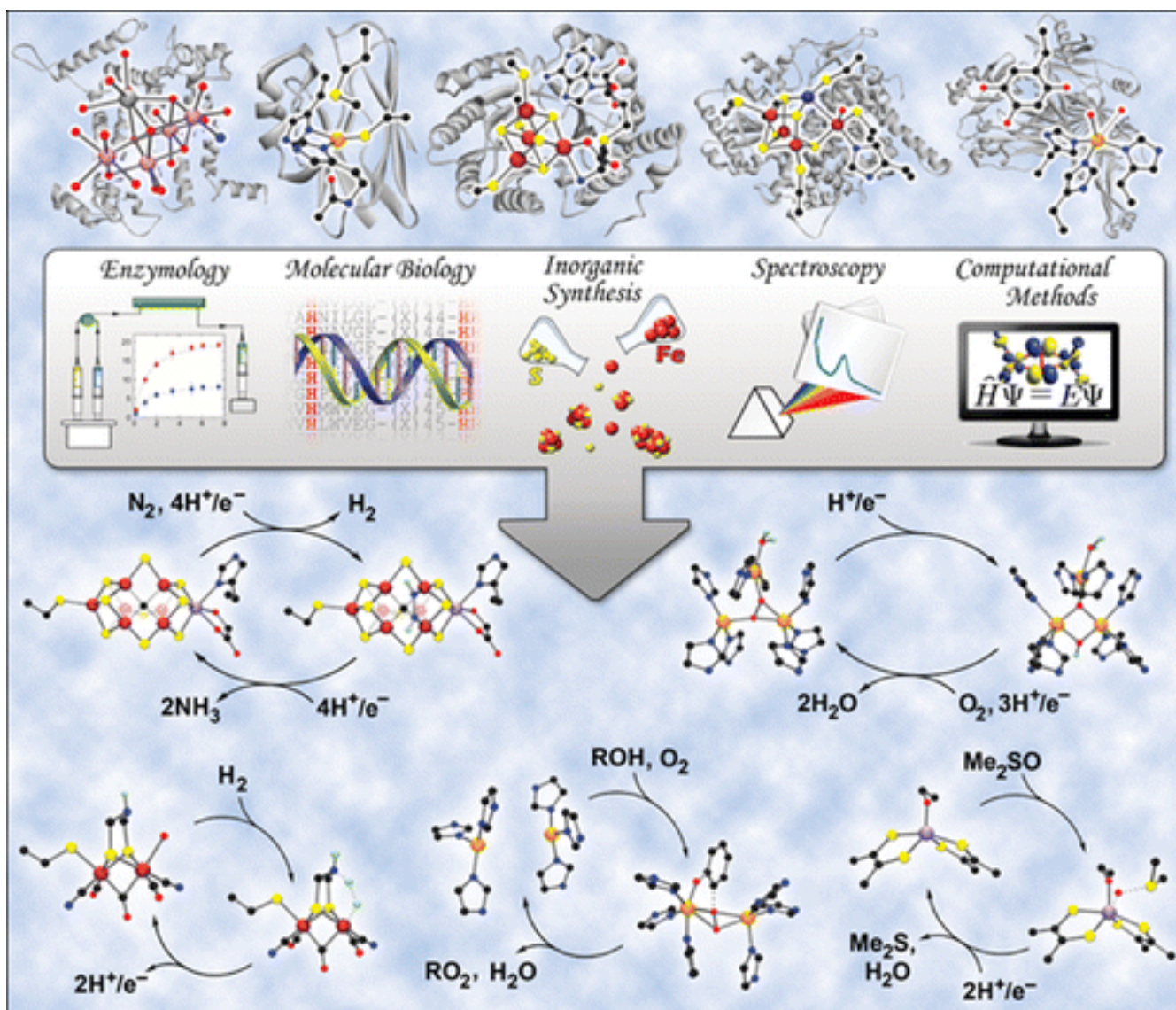




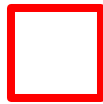
12 elementi metallici essenziali

s-block elements

d-block elements

p-block elements

Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57–71 La–Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89–103 Ac–Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub						



Bulk Metals



Trace



Ultra-trace

f-block elements

Lanthanoids	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinoids	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Metal	g/75 kg
Na	70 – 120
K	160 – 200
Ca	1100
Mg	25
Fe	4 – 5
Zn	2 – 3
Cu	$80 - 120 \times 10^{-3}$
V	15×10^{-3}
Mn	1×10^{-2}
Co	1.2×10^{-3}
Mo	10×10^{-3}
Ni	?

Average
intracellular
concentration:

$[\text{Fe}]_{\text{total}} = 0.5 \text{ mM}$

$[\text{Zn}]_{\text{total}} = 0.5 \text{ mM}$

$[\text{Cu}]_{\text{total}} = 50 \text{ } \mu\text{M}$

Metalloma

Ogni specie è caratterizzata da uno specifico

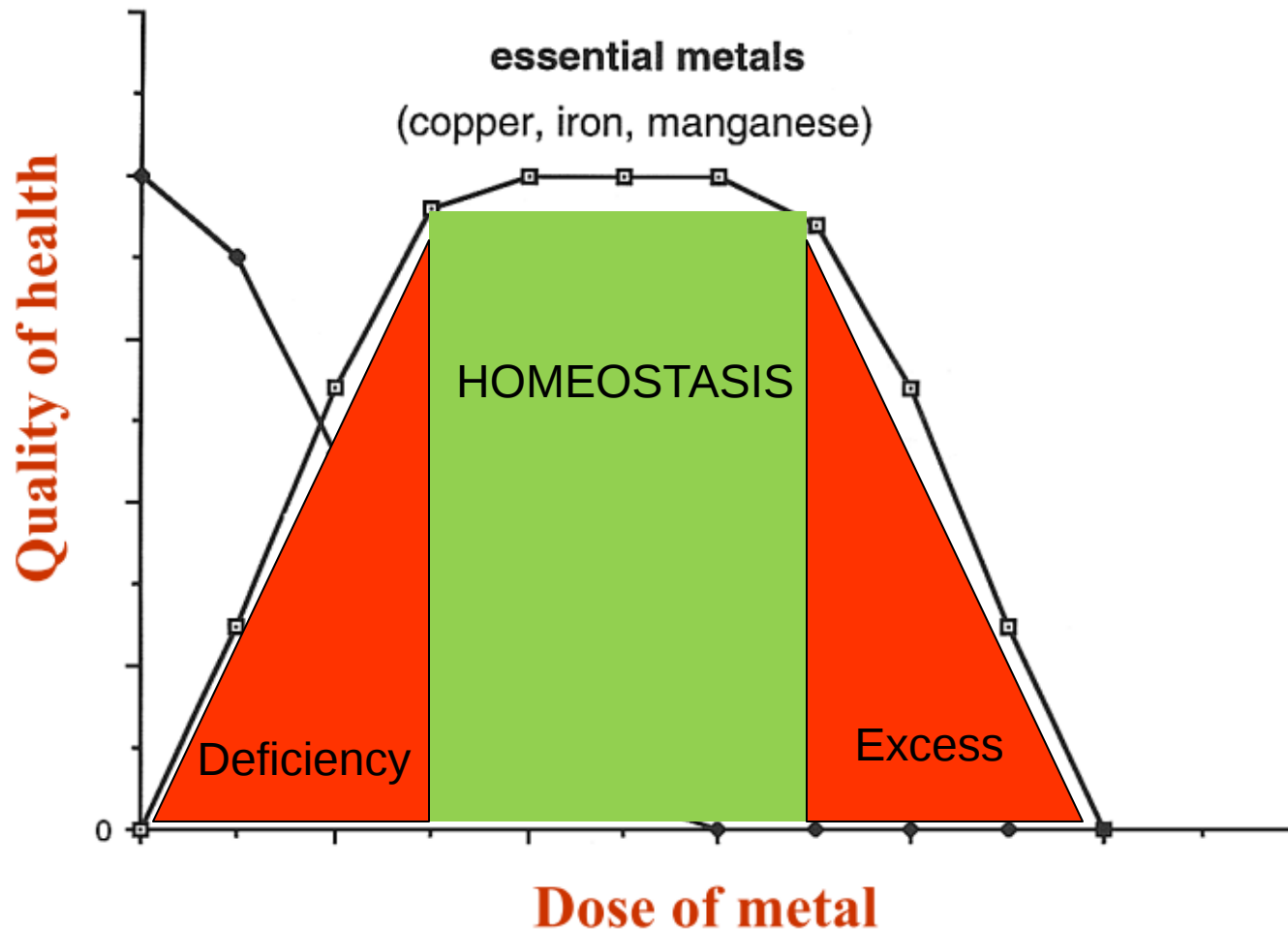
metalloma

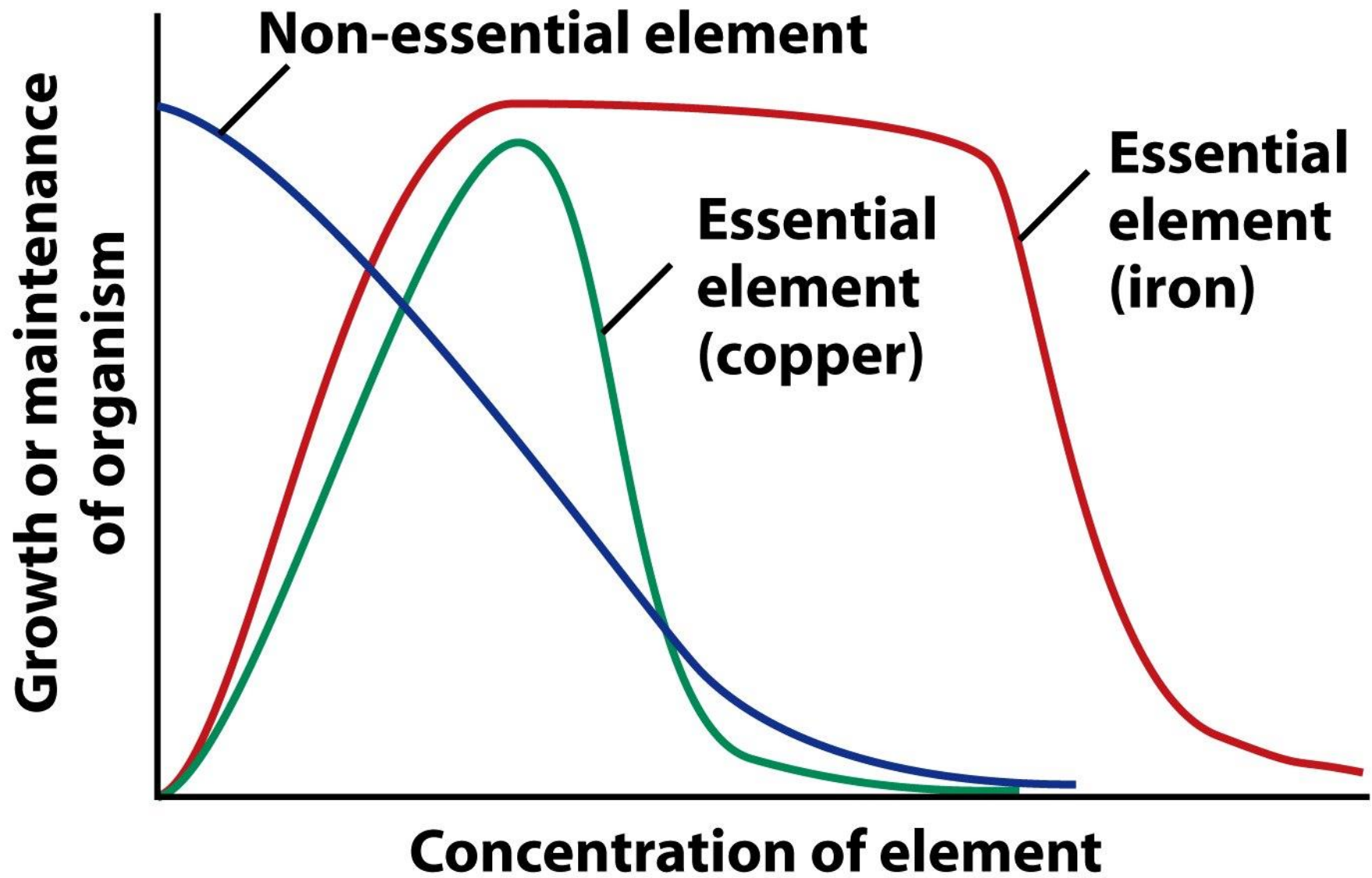
definito come l'insieme di metalli contenuto in ogni tipo di cellula di quella specie, ognuno con la sua specifica **quantità, speciazione e localizzazione** all'interno di ogni cellula

Come si stabilisce se un elemento è essenziale per una specie?

Si definisce **essenziale** un elemento sistematicamente presente in una certa specie biologica e tale che la sua assenza (o carenza) nelle fonti nutritive di quella specie sia causa di malattie, disturbi metabolici o dello sviluppo

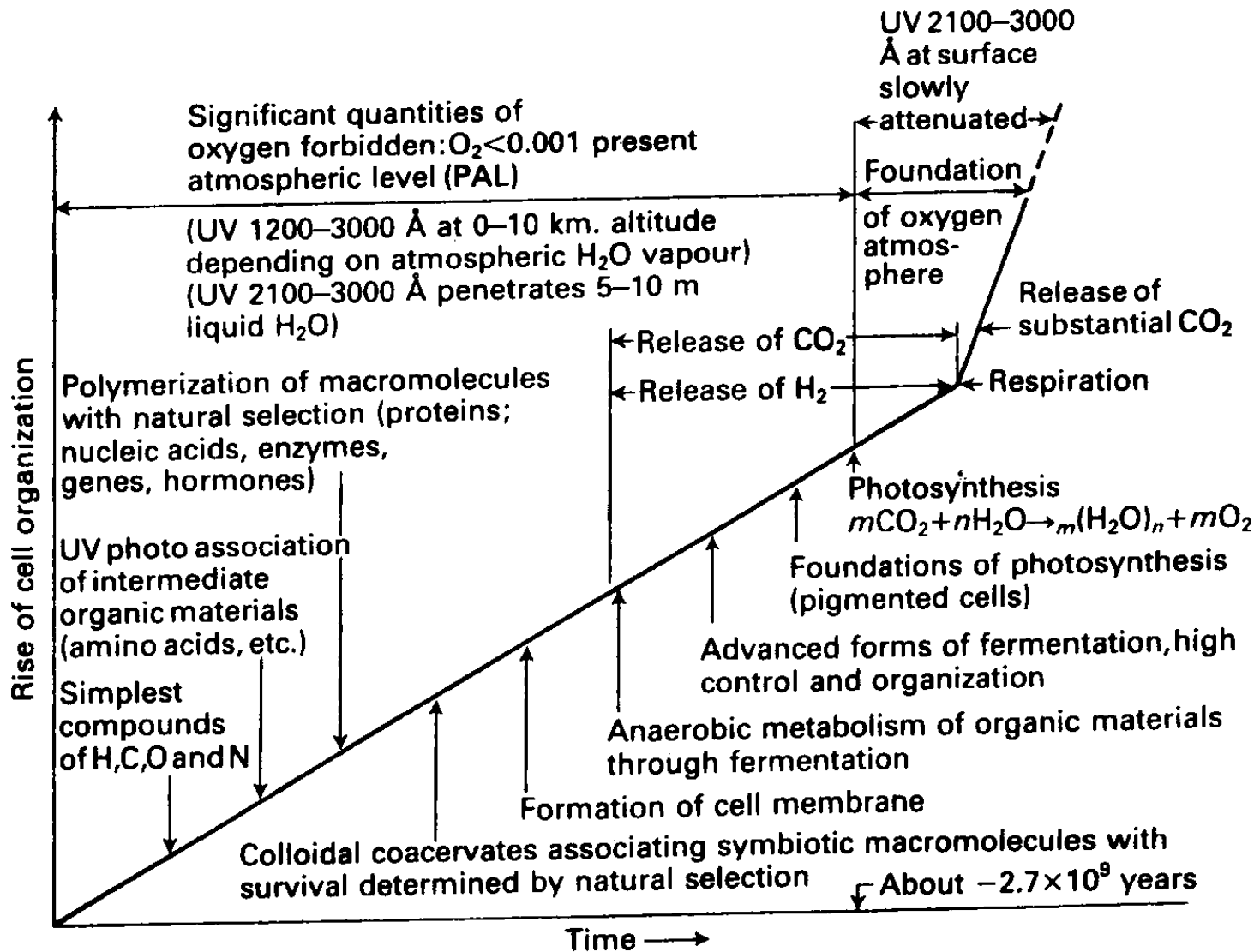
Dose-response curve





Elemento	Sintomi da deficienza	Sintomi da eccesso
Ca	Ritardo nella crescita dello scheletro	
Mg	Crampi muscolari, convulsioni	
Fe	Anemia, disordini nel sistema immunitario	Stress ossidativo
Zn	Danni alla pelle, ritardata maturazione sessuale	
Cu	Debolezza delle arterie, disordini del fegato, anemia secondaria, Sindrome di Menkes	Sindrome di Wilson
Mn	Infertilità, ridotta crescita dello scheletro	Disturbi psichiatrici
Mo	Ritardo nella crescita delle cellule, propensione alla carie	Anemia
Co	Anemia perniziosa	Disturbi cardiaci
Si	Disordini nella crescita dello scheletro	
F	Carie	
I	Gotta, disordini tiroidei, metabolismo ritardato	Gotta
Se	Debolezza muscolare, cardiomiopatia	
As	Crescita ritardata	

Biodisponibilità degli elementi



Potenziali redox accessibili in acqua a pH 7: fra -0.4 V (H^+/H_2) e $+0.8 \text{ V}$ (O_2/OH^-)

Potenziali redox primordiali in acqua a pH 7: fra -0.4 V (H^+/H_2) e ca. 0.0 V ($\text{S}_n/\text{H}_2\text{S}$)

Elemento	Ambiente riducente	Ambiente ossidante
Fe	Fe(II), (alta)	Fe(III), (bassa)
Cu	Come solfuro (bassa)	Cu(II), (moderata)
S	HS^- (alta)	SO_4^{2-} (alta)
Mo	MoS_2 , $(\text{MoO}_n\text{S}_{4-n})^{2-}$ (bassa)	MoO_4^{2-} (moderata)
V	V^{3+} , solfuri di V(IV) (moderata)	VO_4^{3-} (moderata)

Orizzonti ferriferi a bande



Ruoli dei metalli nei sistemi biologici

Ruolo strutturale

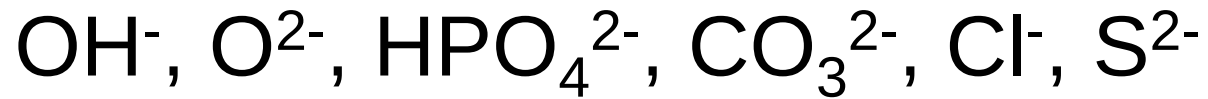
Endo- ed esoscheletri, stabilizzazione di DNA, RNA e proteine

Ruolo funzionale

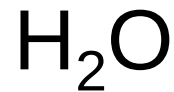
- Trasporto di carica
- Sintesi e metabolismo di molecole organiche
- Trasferimento di elettroni
- Attivazione di piccole molecole
- Reattività organometallica

Biological ligands

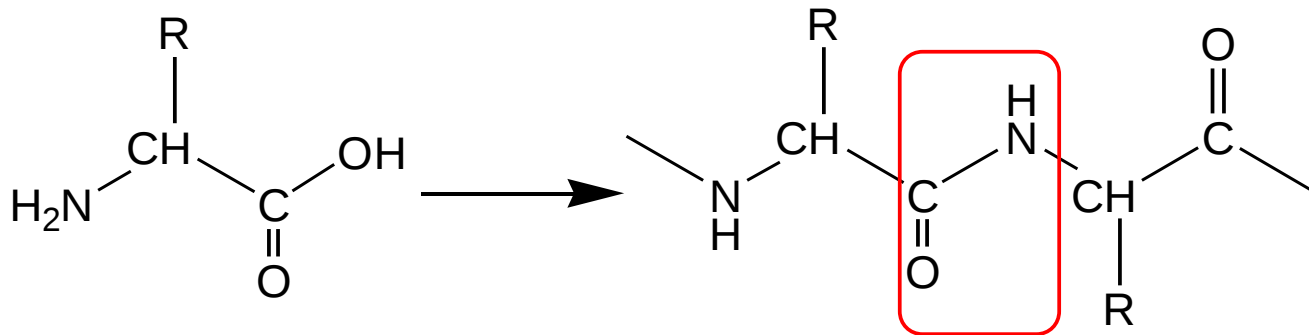
Anions



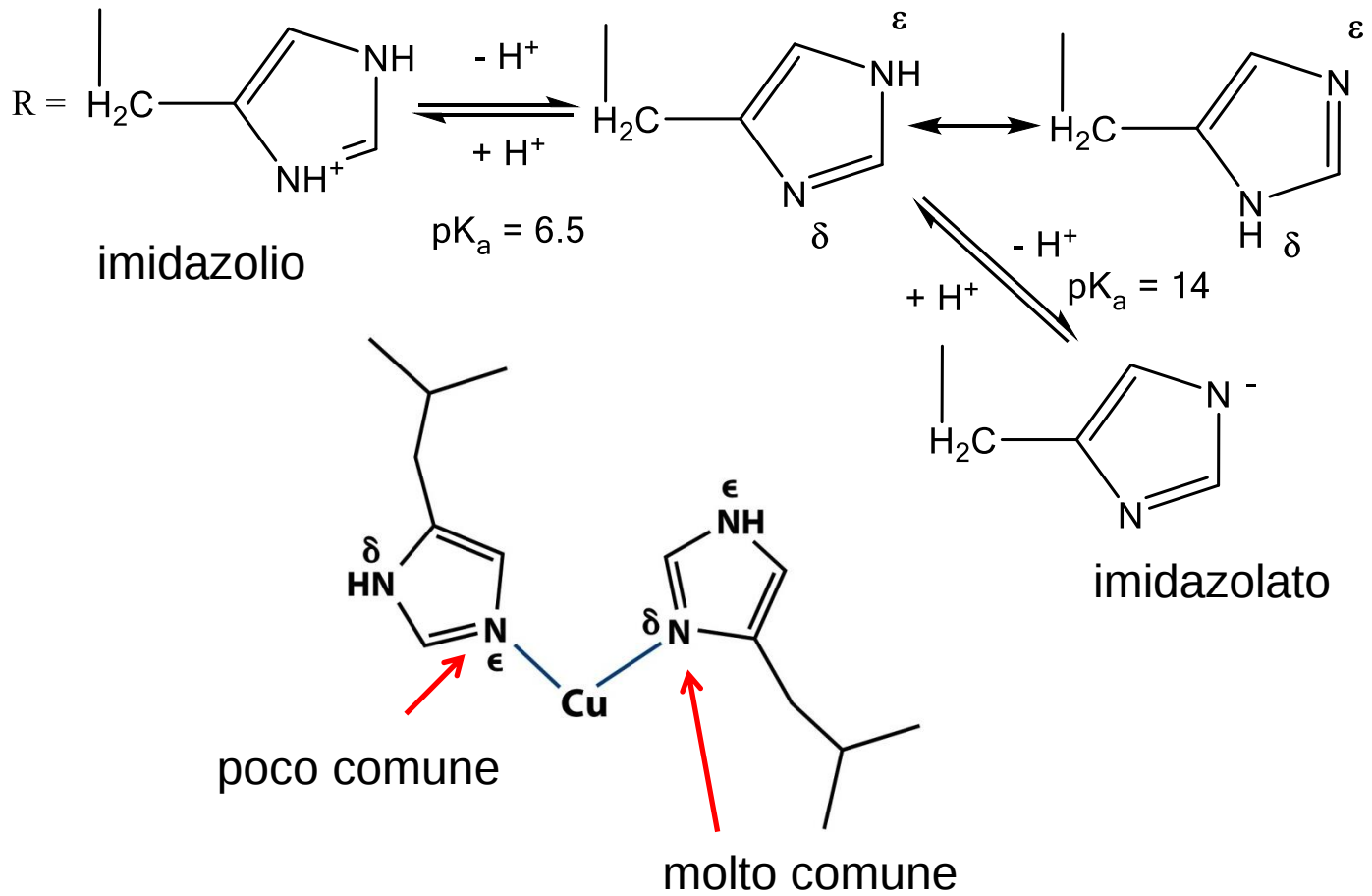
Water



Aminoacid side-chains

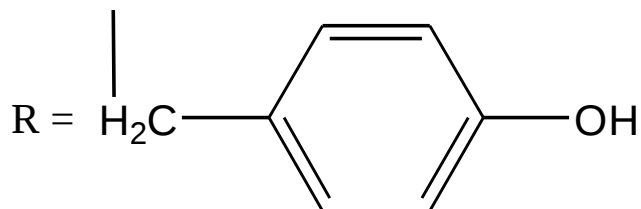


Istidina (His)

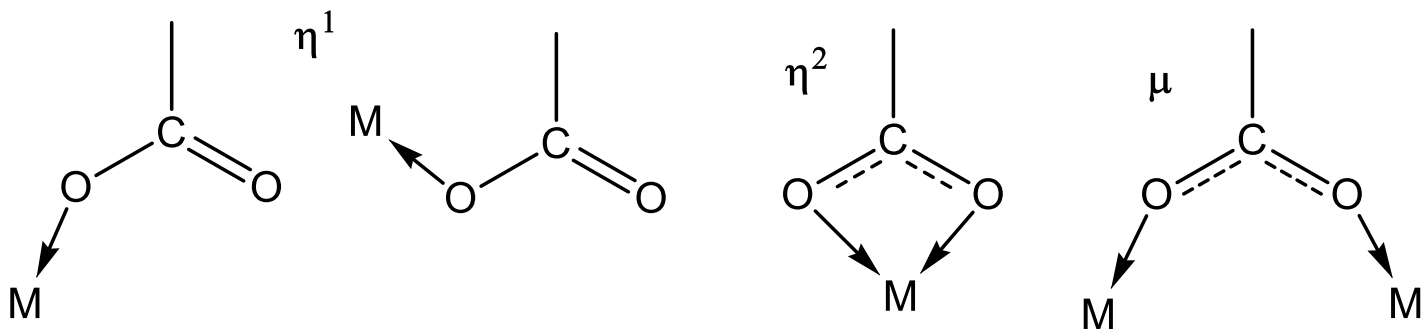


$R = \text{CH}_2\text{SH}$
 Cisteina (Cys), $\text{pK}_a = 8.5$

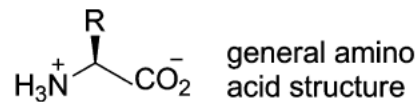
$R = -\text{CH}_2\text{CH}_2\text{SCH}_3$
 Metionina (Met)



Tirosina, $\text{pK}_a = 10$



Glutammato (Glu): $R = -\text{CH}_2\text{CH}_2\text{COO}^-$ Aspartato (Asp): $R = -\text{CH}_2\text{COO}^-$
 $\text{pK}_a = 4.5$

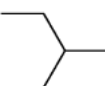


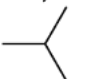
Amino acids with non-polar side chains:

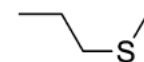
Gly R = —H

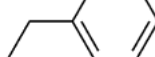
Ala R = —

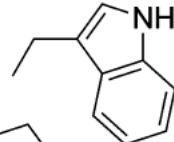
Val R = 

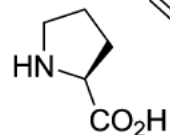
Leu R = 

Ile R = 

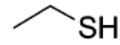
Met R = 

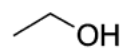
Phe R = 

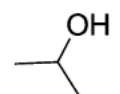
Trp R = 

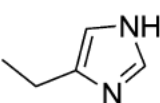
Pro 

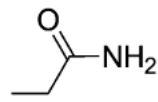
Amino acids with polar side chains:

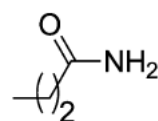
Cys R = 

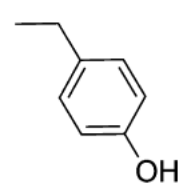
Ser R = 

Thr R = 

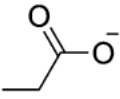
His R = 

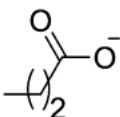
Asn R = 

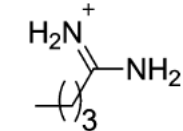
Gln R = 

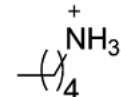
Tyr R = 

Amino acids with charged polar side chains:

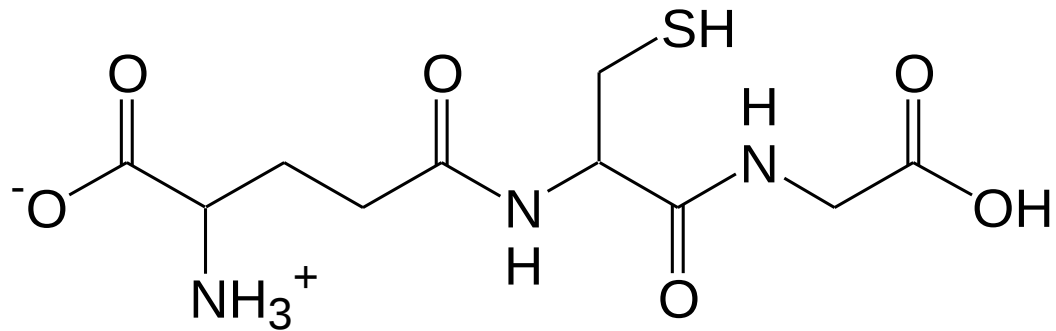
Asp R = 

Glu R = 

Arg R = 

Lys R = 

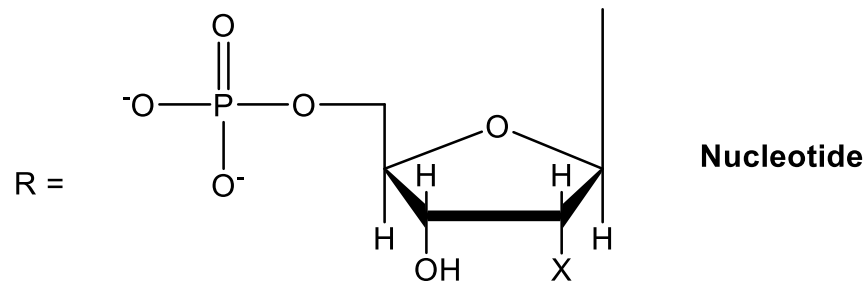
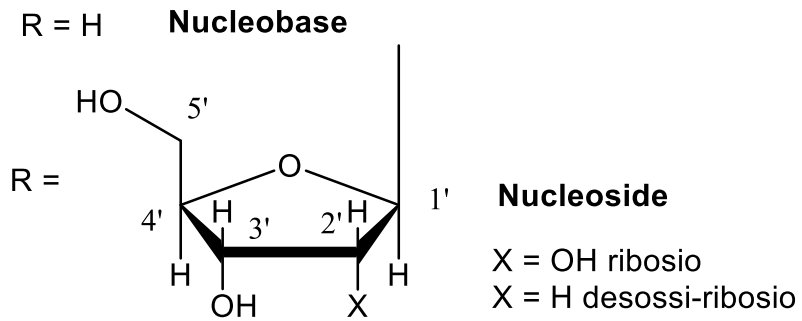
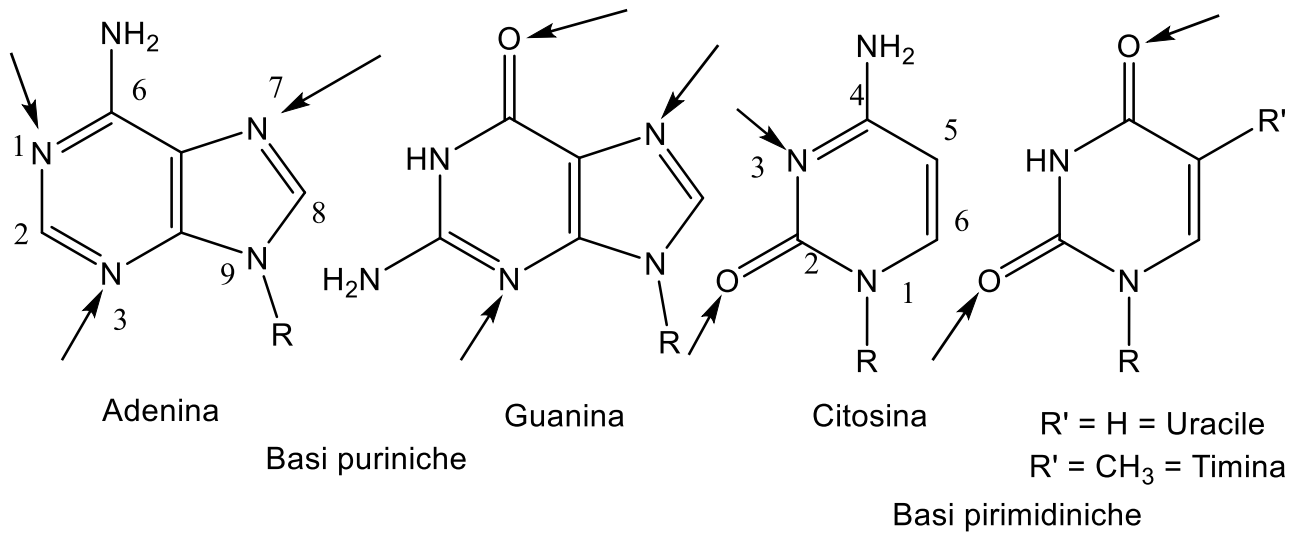
GLUTATIONE

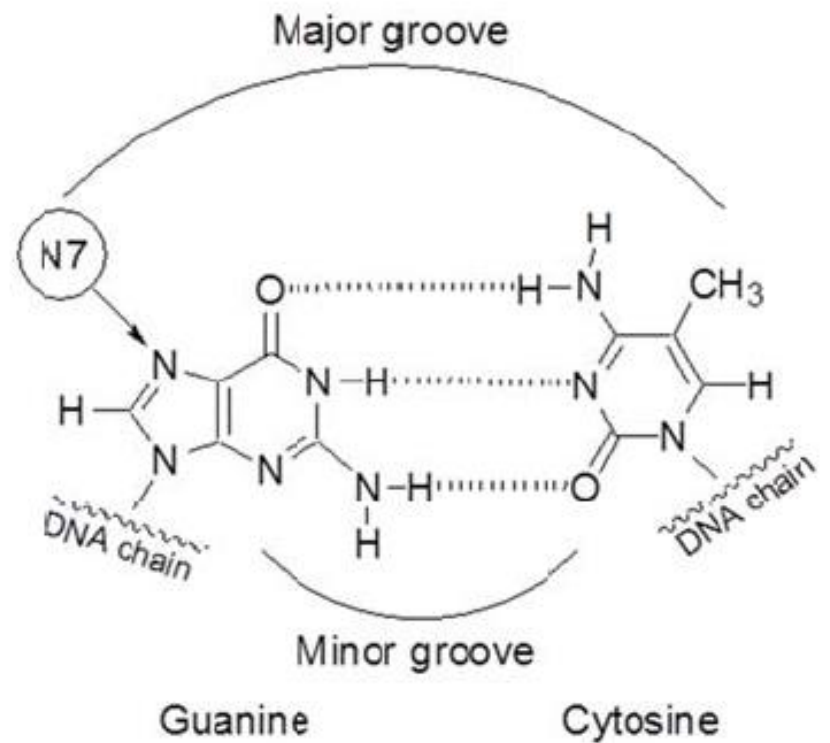
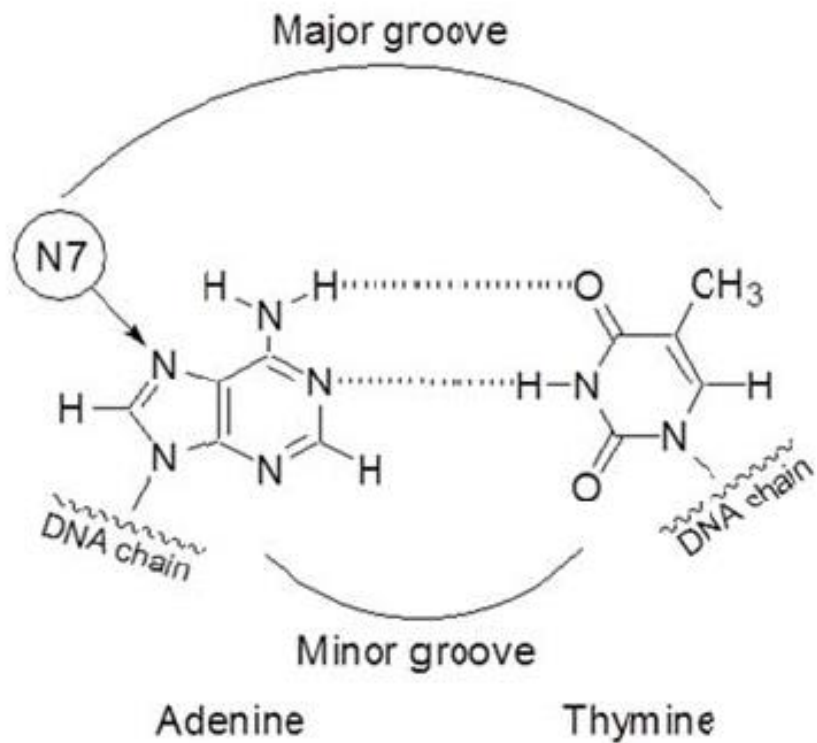


GSH

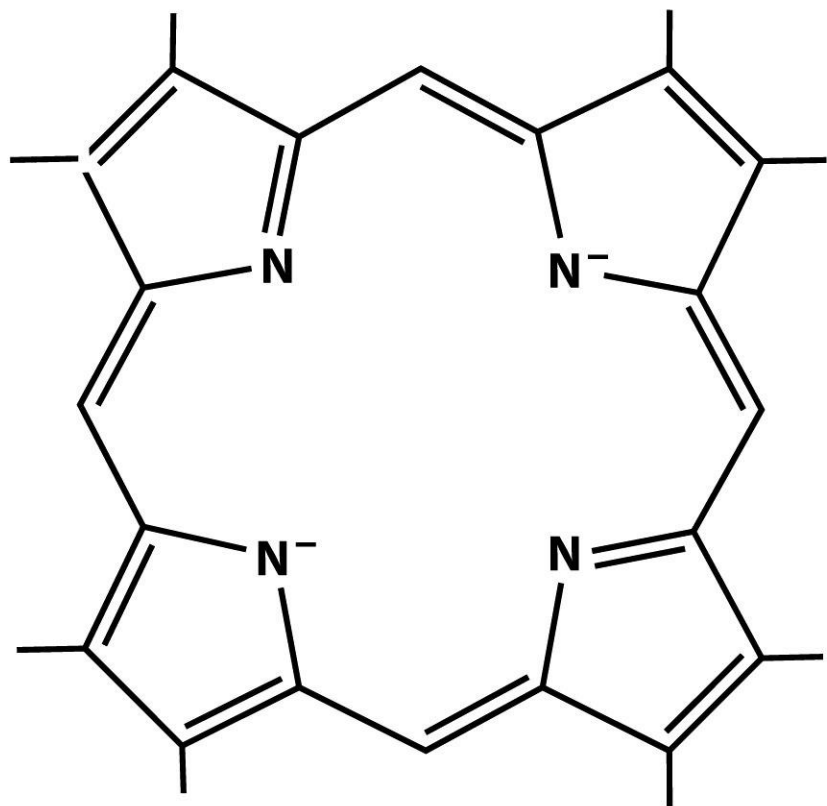
Glu-Cys-Gly

0.5 – 10 mM intracellulare
(riducente monoelettronico)

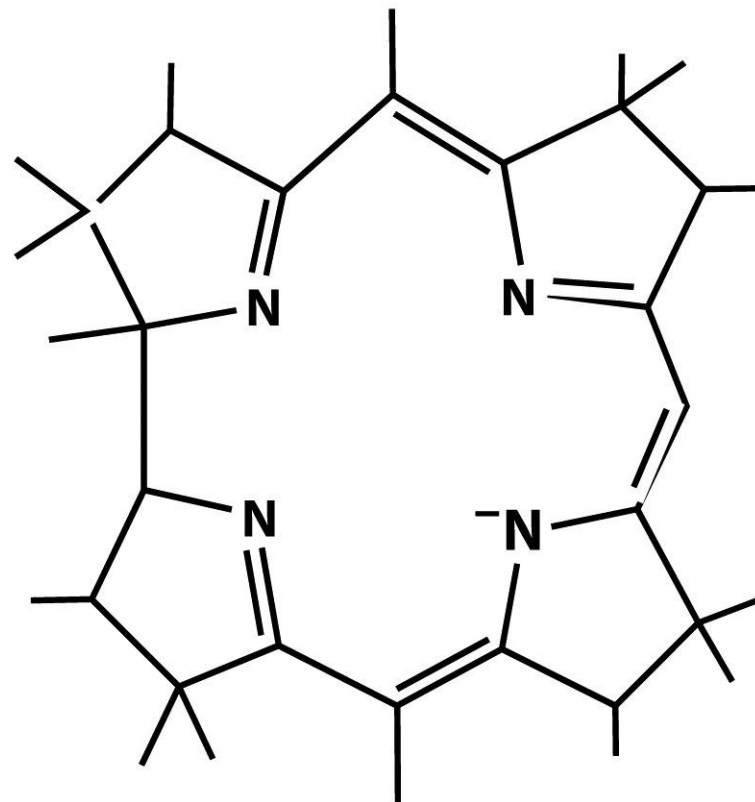




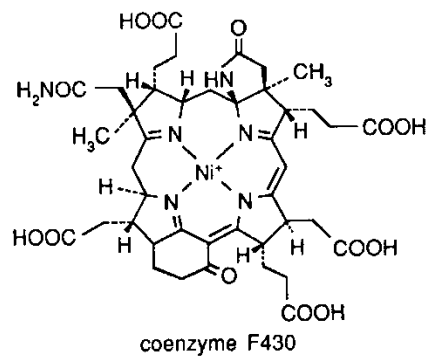
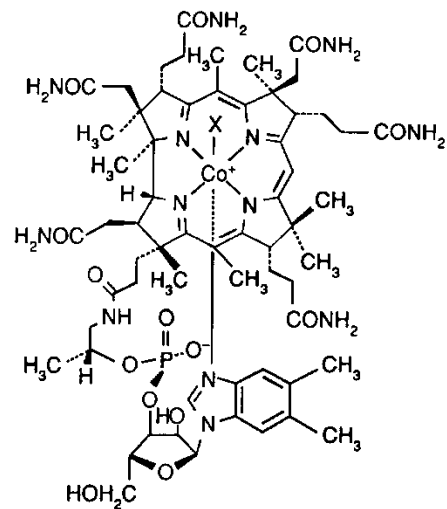
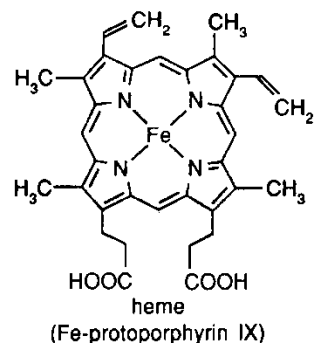
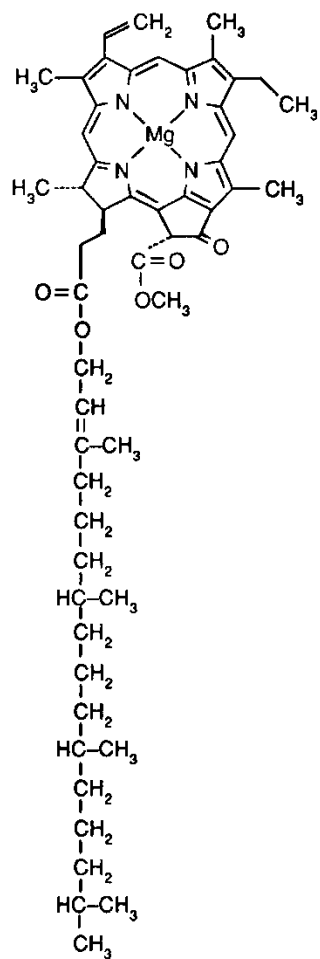
Leganti tetrapirrolici



Porphyrin²⁻



Corrin⁻



Endogenous reducing agents

Electron transfer enzymes

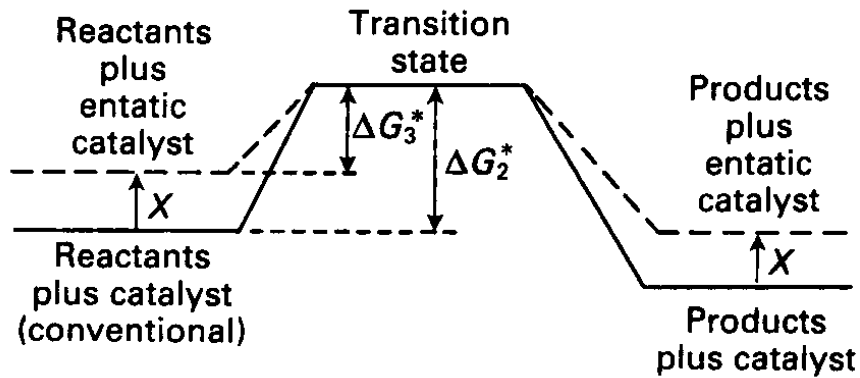
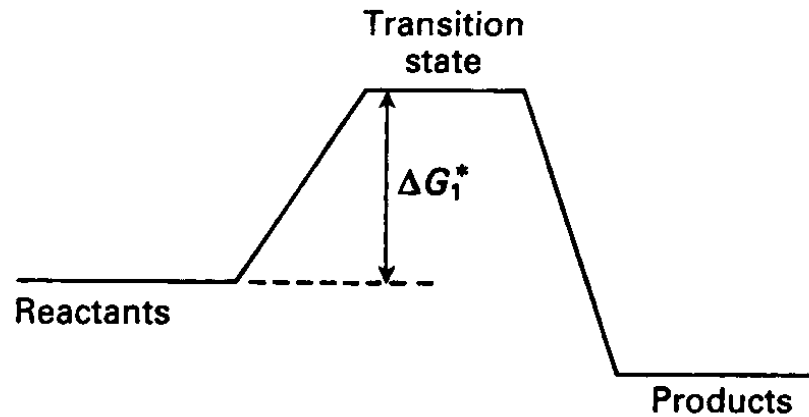
Ascorbic acid: 11–79 μM in the blood

Glutathione: 0.5 – 10 mM intracellular

Table 2.6 Typical coordination environments of metal centers in proteins

metal oxidation state	bond stability	typical number and type of side chain ligands	typical coordination geometry
Zn(II)	high	3: His, Cys ⁻ , (Glu ⁻)	severely distorted tetrahedron
Cu(I)	high	3,4: His, Cys ⁻ , Met	severely distorted tetrahedron
Cu(II)	high	3,4: His, (Cys ⁻)	distorted square planar arrangement
Fe(II), Ni(II) Co(II), Mg(II)	low	4-6: His, Glu ⁻ , Asp ⁻	distorted octahedron
Fe(III)	high	4-6: Glu ⁻ , Asp ⁻ , Tyr ⁻ , Cys ⁻	distorted octahedron

Stato entatico



Stato entatico

