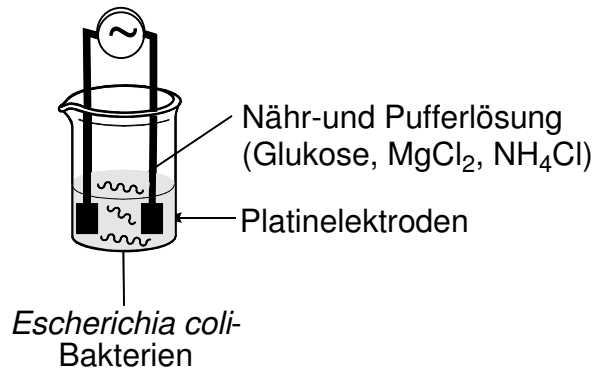
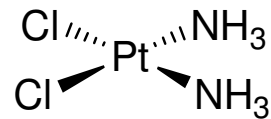
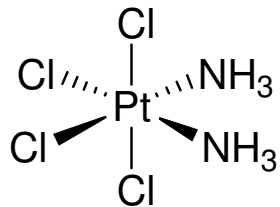


Bio und Anorganik ?

Rosenberg-Versuch

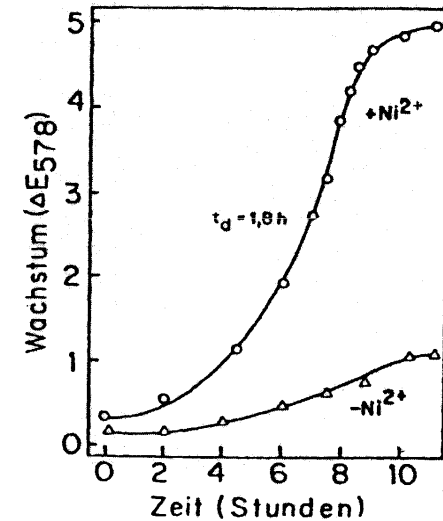
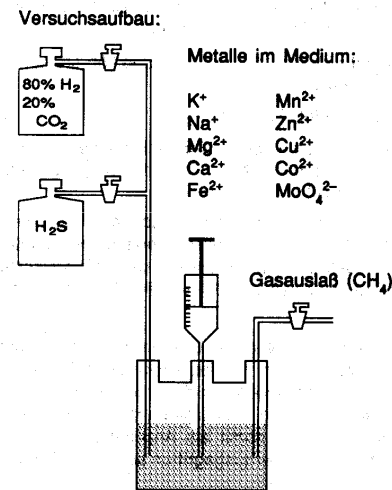
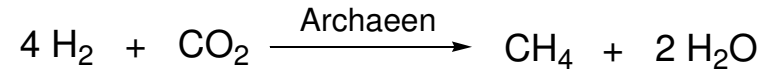


→ cytostatische Wirkung durch
8 ppm Platin in Lösung



Cisplatin

Thauer-Versuch



Abhängigkeit des Bakterienwachstums
von der Eintauchtiefe der Kanüle

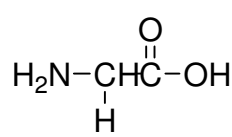
→ Edelstahlkanüle: 70 % Eisen
20 % Chrom
10 % Nickel

Metallionen der Bioanorganik

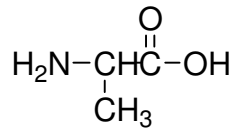
	I	II	Nebengruppenelemente										III	IV	V	VI	VII	VIII	
1	1 H 1.006																		2 He 4.003
2	3 Li 6.94	4 Be 9.01												5 B 10.81	6 C 12.011	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31												13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80	
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30	
6	55 Cs 132.91	56 Ba 137.34	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.96	84 Po (209)	85 At (210)	86 Rn (222)	
Lanthaniden		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97				
Actiniden		90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (249)	99 Es (254)	100 Fm (257)	101 Md (258)	102 No (255)	103 Lr (256)				

violett: Mengenelemente, **gelb:** Spurenelemente, **grau:** pharmazeutisch verwendete Elemente

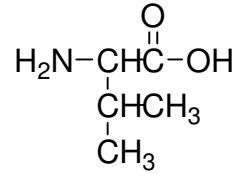
Liganden der Bioanorganik



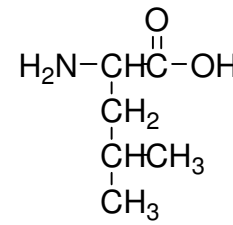
Gly



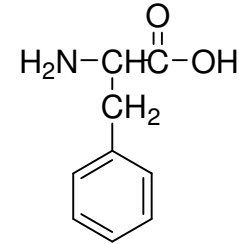
Ala



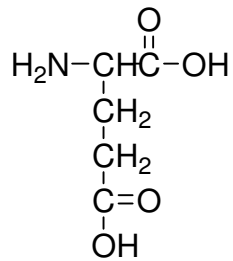
Val



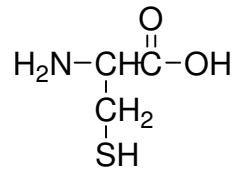
Leu



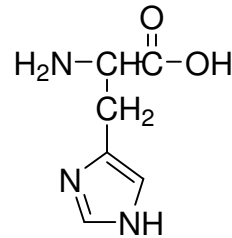
Phe



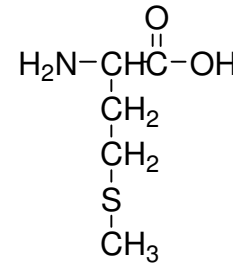
Glu



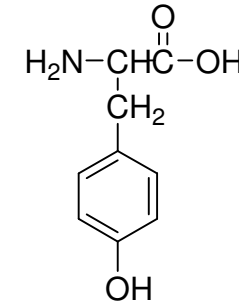
Cys



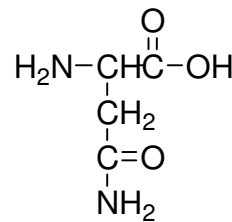
His



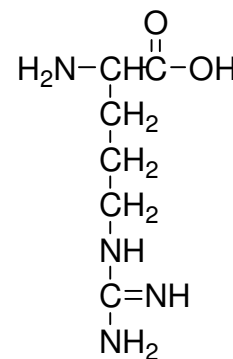
Met



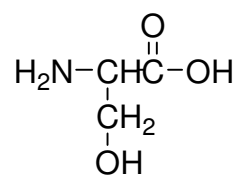
Tyr



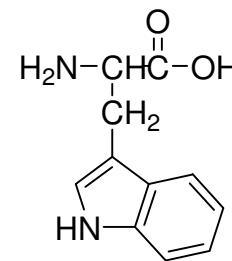
Asn



Arg

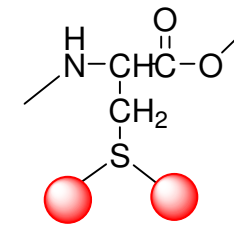
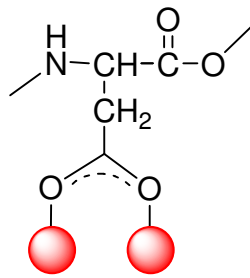
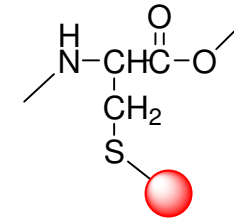
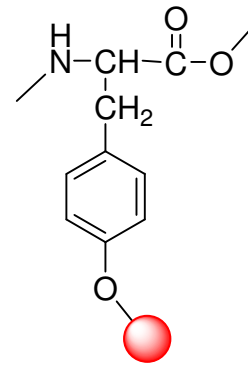
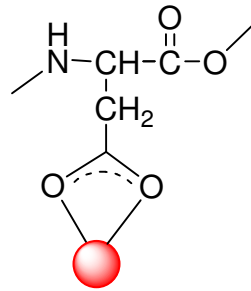
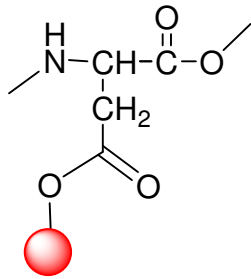
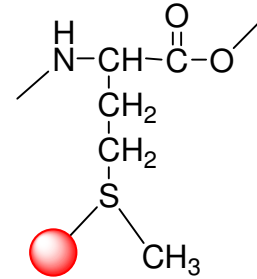
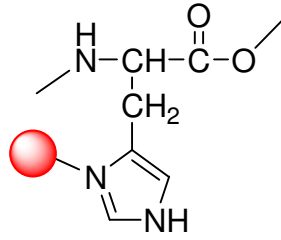
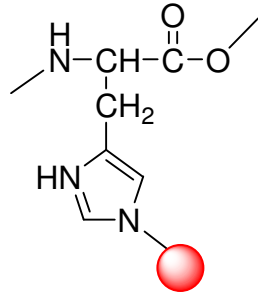


Ser



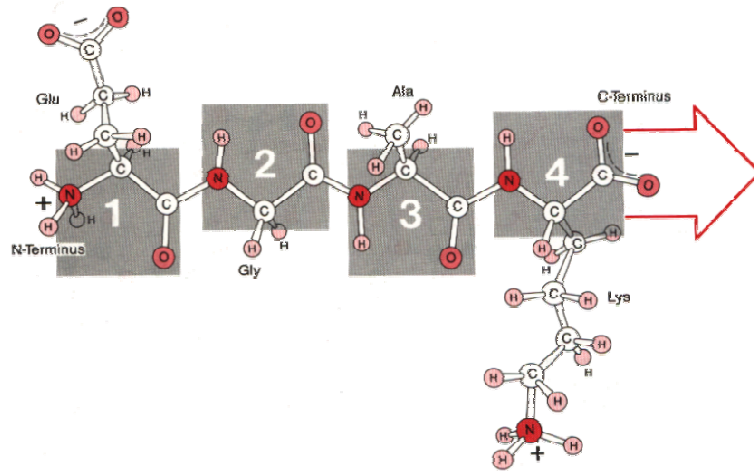
Trp

Koordinationsweisen von Aminosäure-Seitenketten

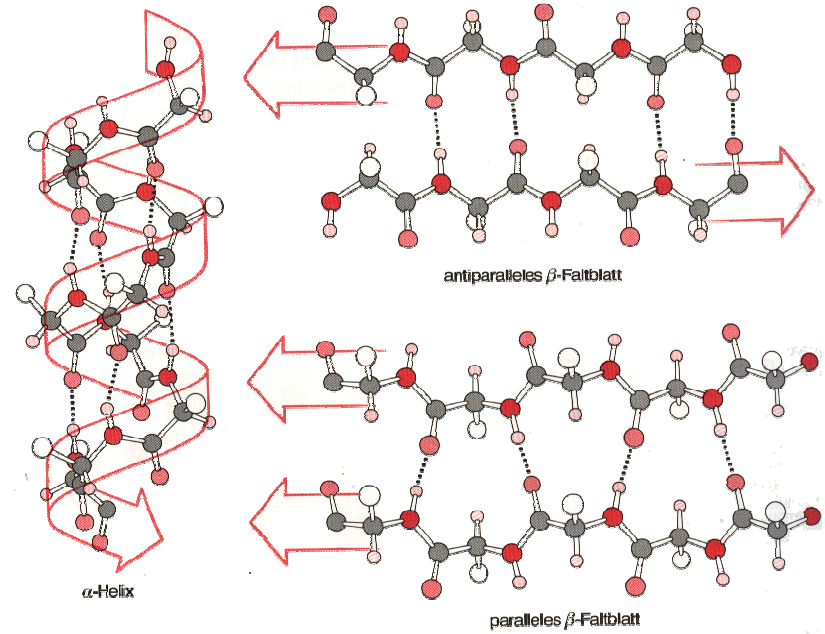


Eiweiß-Grundstruktur

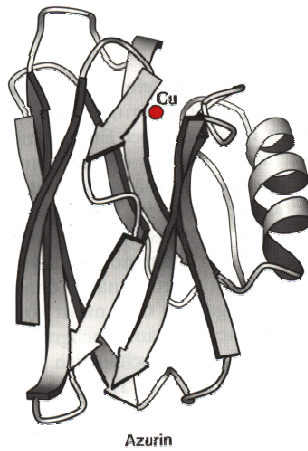
Primärstruktur



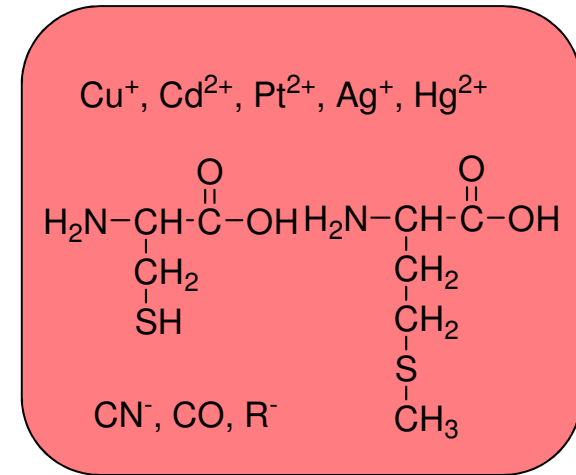
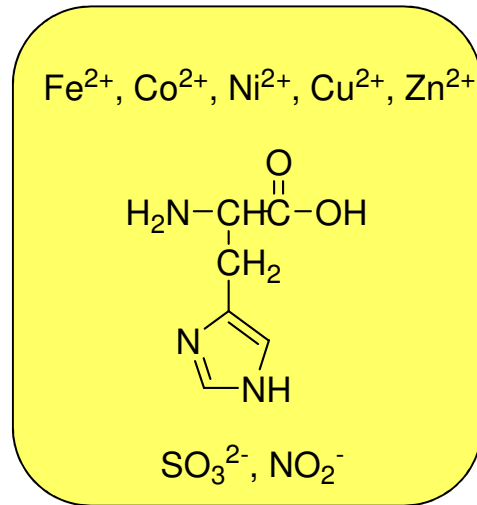
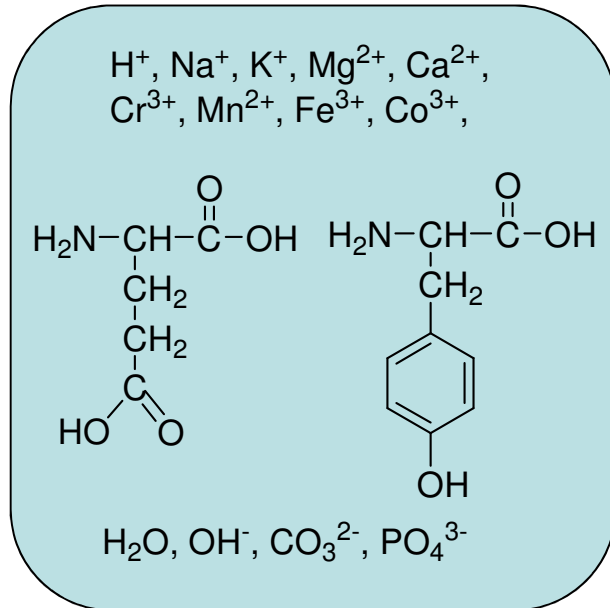
Sekundärstruktur



Tertiärstruktur



Prinzipien der Komplexchemie: HSAB-Konzept



HSAB...hard and soft acids and bases (nach Pearson)

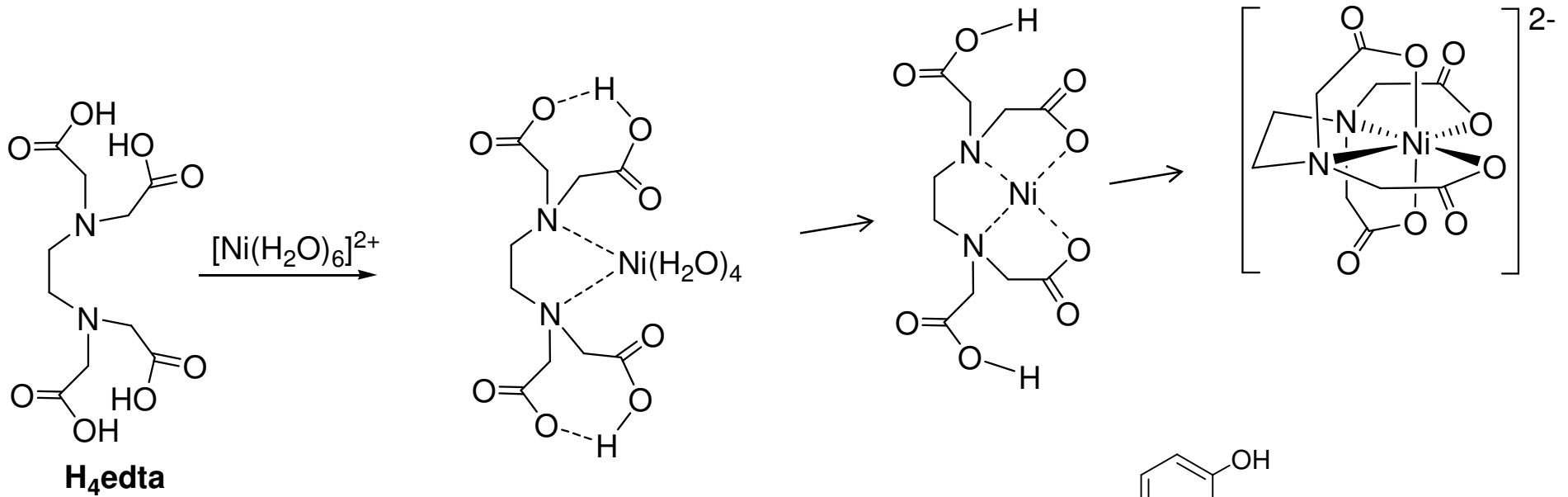
weich: groß und leicht polarisierbar

hart: klein und wenig polarisierbar

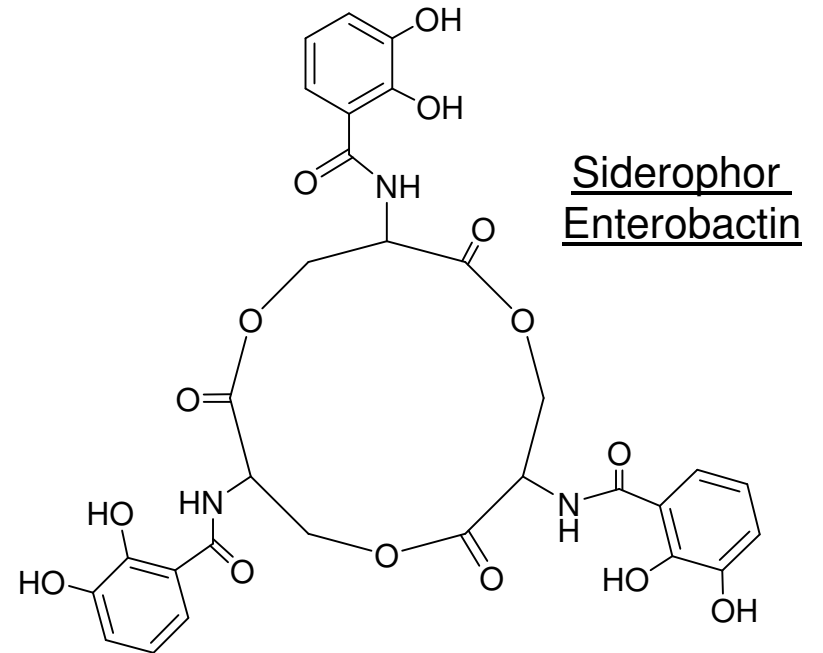
theoretisch-quantitative Ansätze:

- (i) Koordinatensystem aus Ladung/Radius gegen 2. Ionisierungsenergie
- (ii) Bezug zur Größe der HOMO-LUMO-Lücke

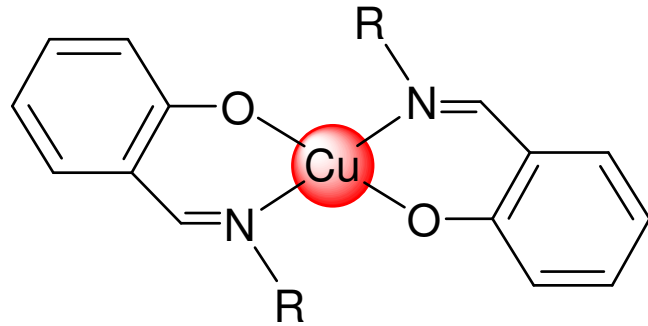
Prinzipien der Komplexchemie: Chelateffekt



Ursache der hohen Stabilität:
 Entropiegewinn (thermodynamisch)
 Konzept der lokalen Konzentration
 (kinetisch)

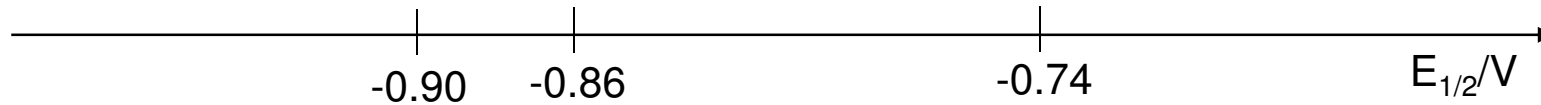


Regulation des Redoxpotentials



Cu(I) → tetraedrische Koordination

Cu(II) → quadratisch planare Koordination

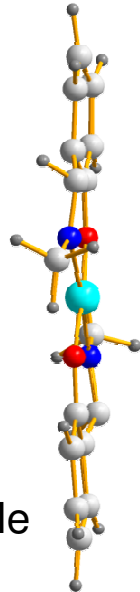


Winkel zwischen
den Chelatringen

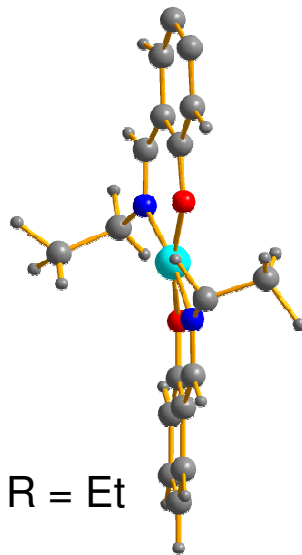
5°

13°

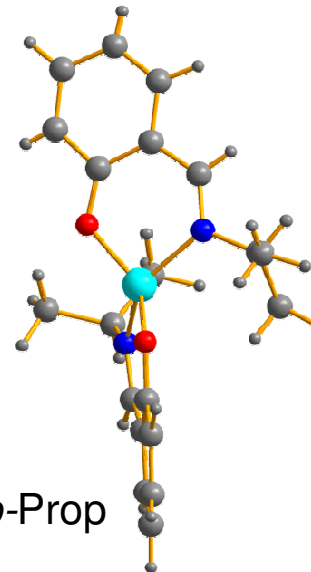
59°



R = Me



R = Et



R = *iso*-Prop

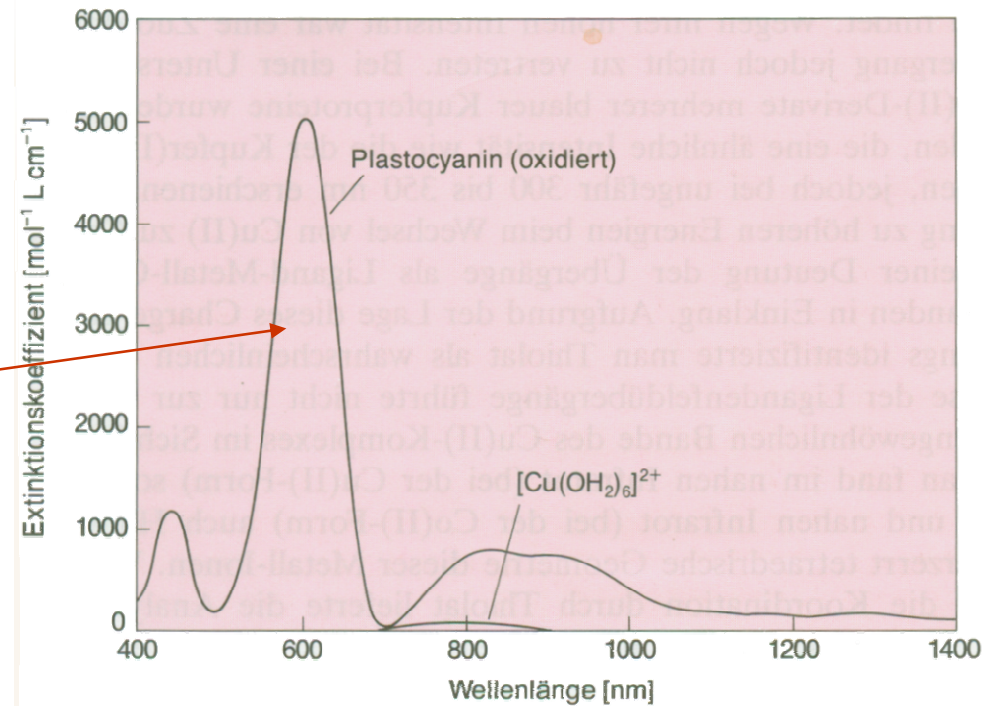
Elektronentransport über Kupfer

Plastocyanin (Azurin)

Molekulargewicht 10500 Da

$E_{1/2} = 370$ mV

Ligand-Metall-Charge-Transfer
vereinbar mit Thiolat-Koordination



EXAFS-Daten

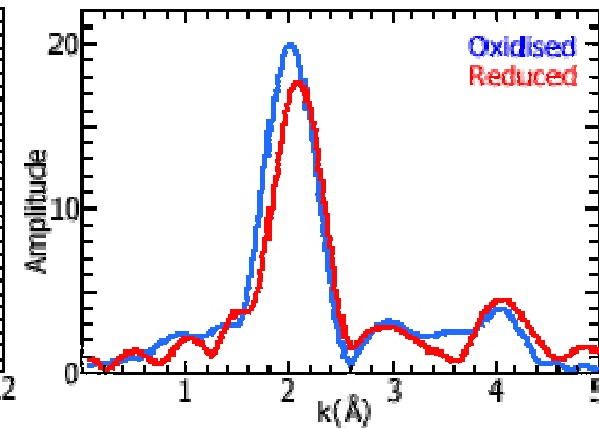
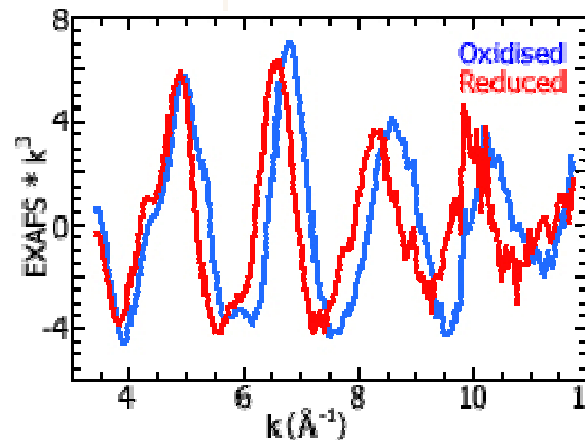
Extended X-ray

Absorption Fine Structure

1 x Histidin,

1 x Thiolat

plus ein weiterer Ligand

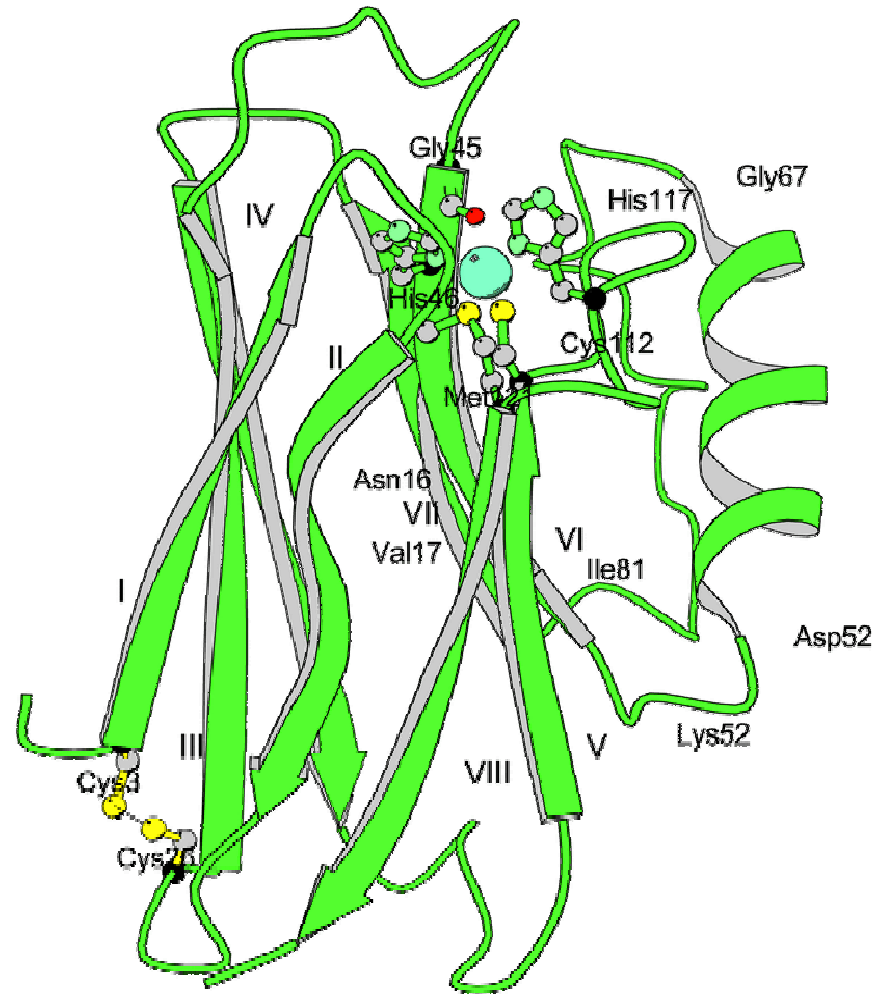
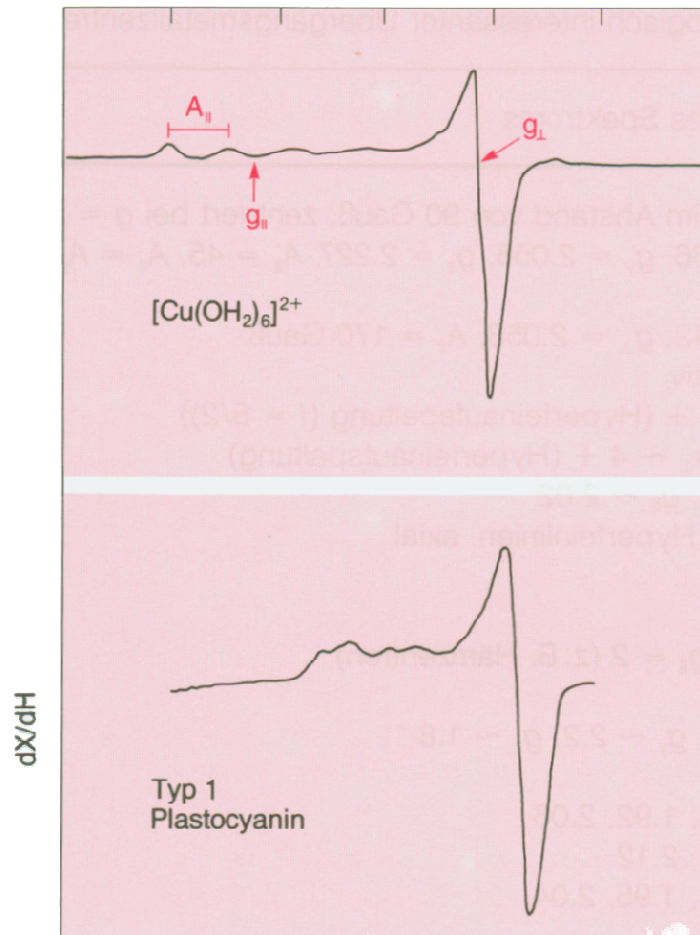


Elektronentransport über Kupfer

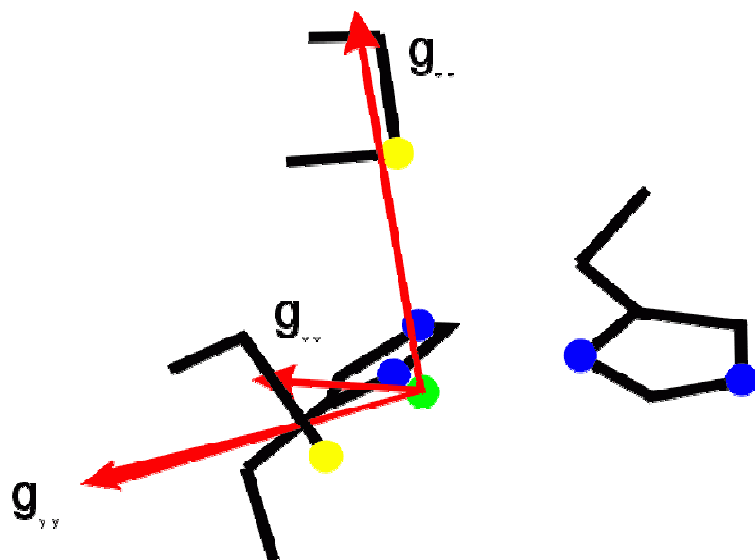
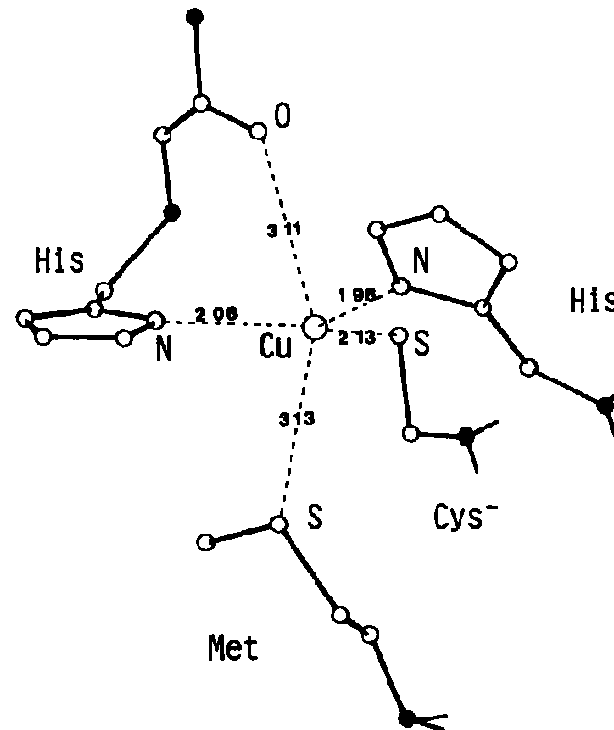
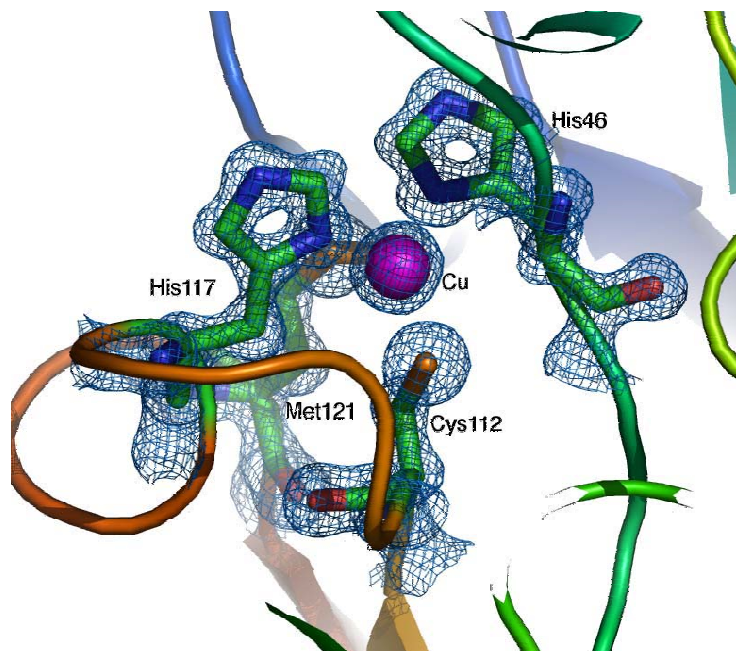
EPR-Spektroskopie

niedrige g-Wert-Anisotropie und kleine Hyperfeinkopplung zu $^{63/65}\text{Cu}$

➔ Delokalisation des einzelnen Elektrons



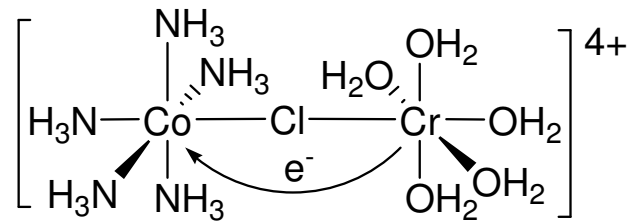
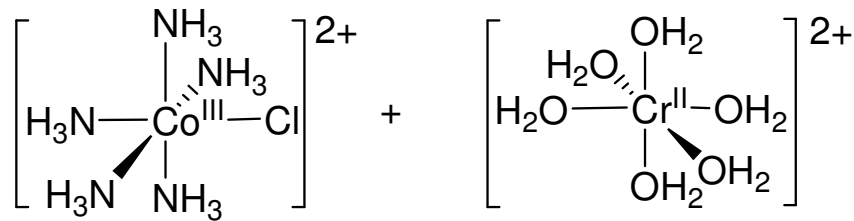
Struktur des aktiven Zentrums des Azurins



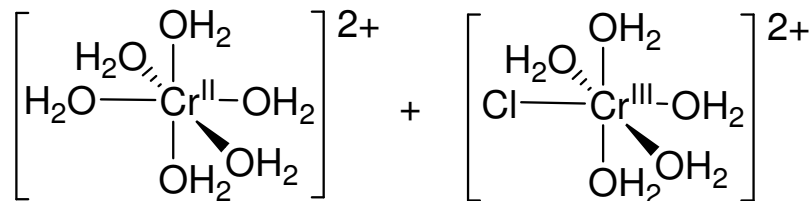
	Cu(II)	Cu(I), pH = 7
Cu - S(Cys)	2.13	2.17
Cu - S(Met)	2.90	2.87
Cu - N(His)	2.04	2.13
Cu - N(His)	2.10	2.39

Kinetische Aspekte: Elektronentransfer

1b. Elektronenübertragung

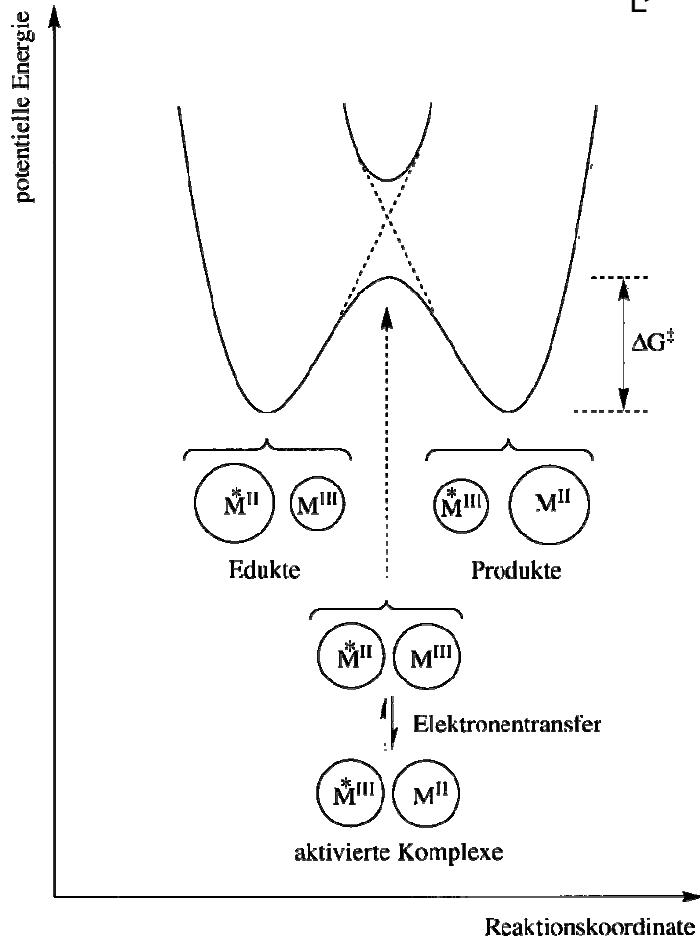
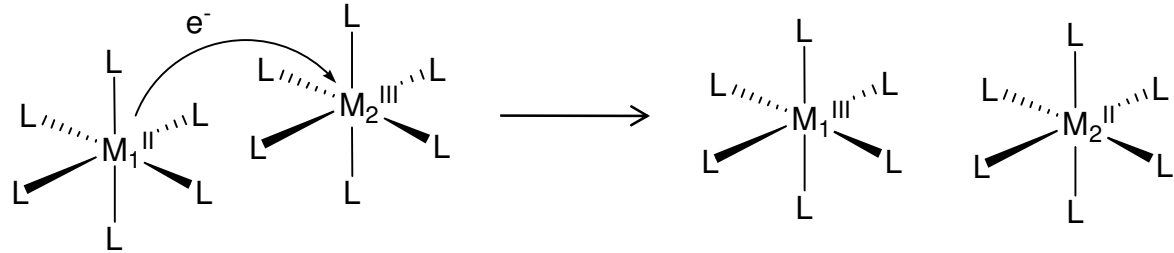


**Innersphere-
Mechanismus**



Kinetische Aspekte: Elektronentransfer

Outersphere-Mechanismus



in vivo verbreitet,
oft keine Brückenliganden vorhanden,
substitutionsträge Komplexe

Frank-Condon-Prinzip:

Schwingungen: ca. 10^{-13} s

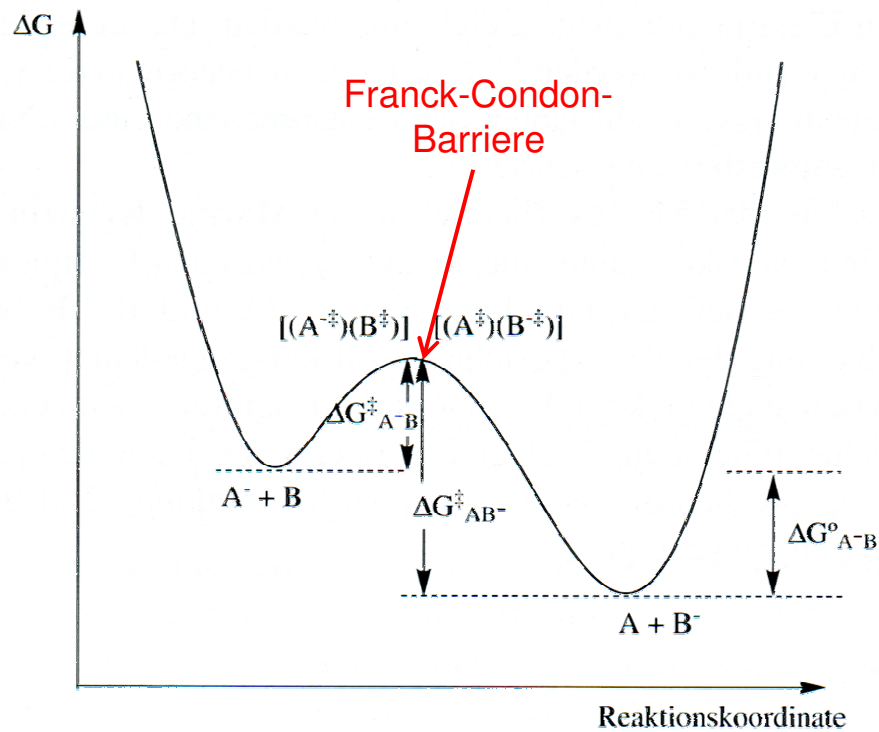
Elektronenübergang: ca. 10^{-15} s

MARCUS-Theorie:

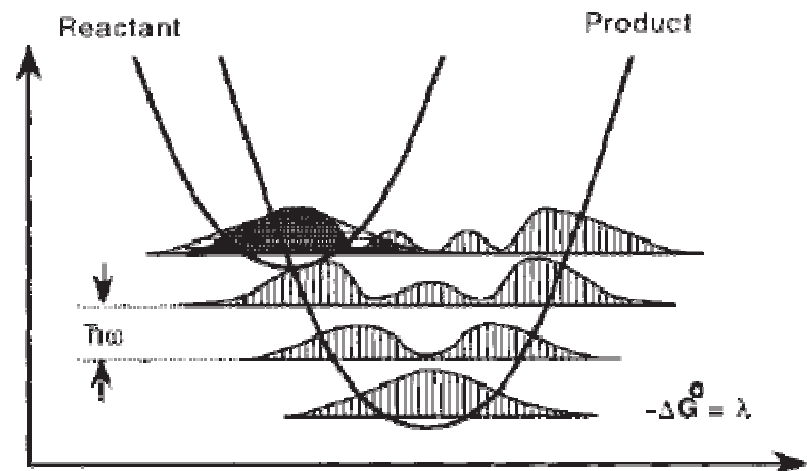
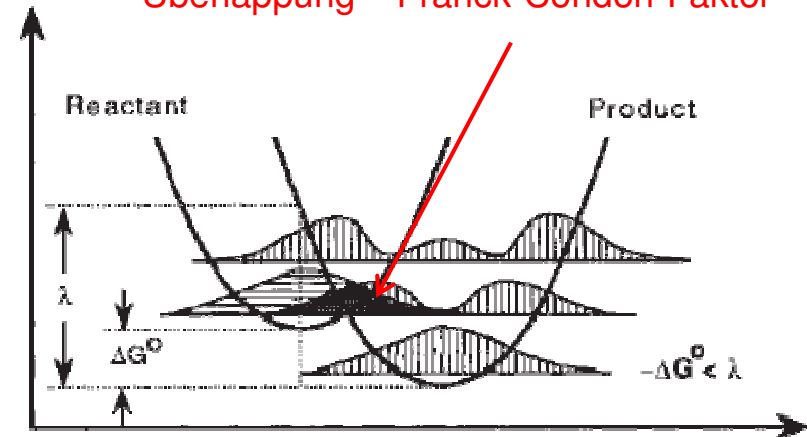
adiabatischer eTransfer nach
Angleichung der Koordinationsgeometrien
Geschwindigkeit des Ladungstransfers
 k_{et} ist Funktion von ΔG und der
Reorganisationsenergie λ

Kinetische Aspekte: Elektronentransfer

Zusammenhang
 ΔG° des eTransfers und
 Reorganisationsenergie λ

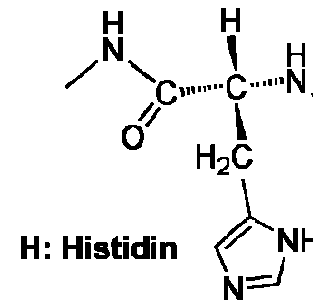
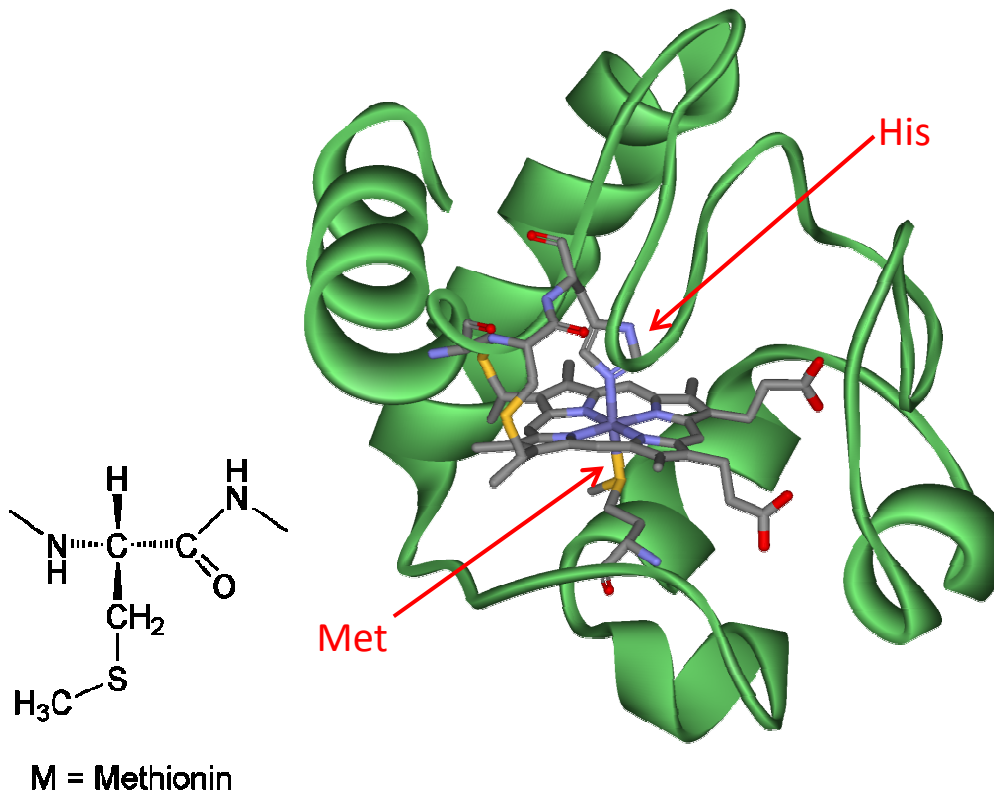


Überlappung ~ Franck-Condon-Faktor



Elektronentransfer: Cytochrome

Cytochrom c: kleines Protein (ca. 100 Aminosäuren)
Vorkommen: Mitochondrien („Kraftwerk der Zelle“)

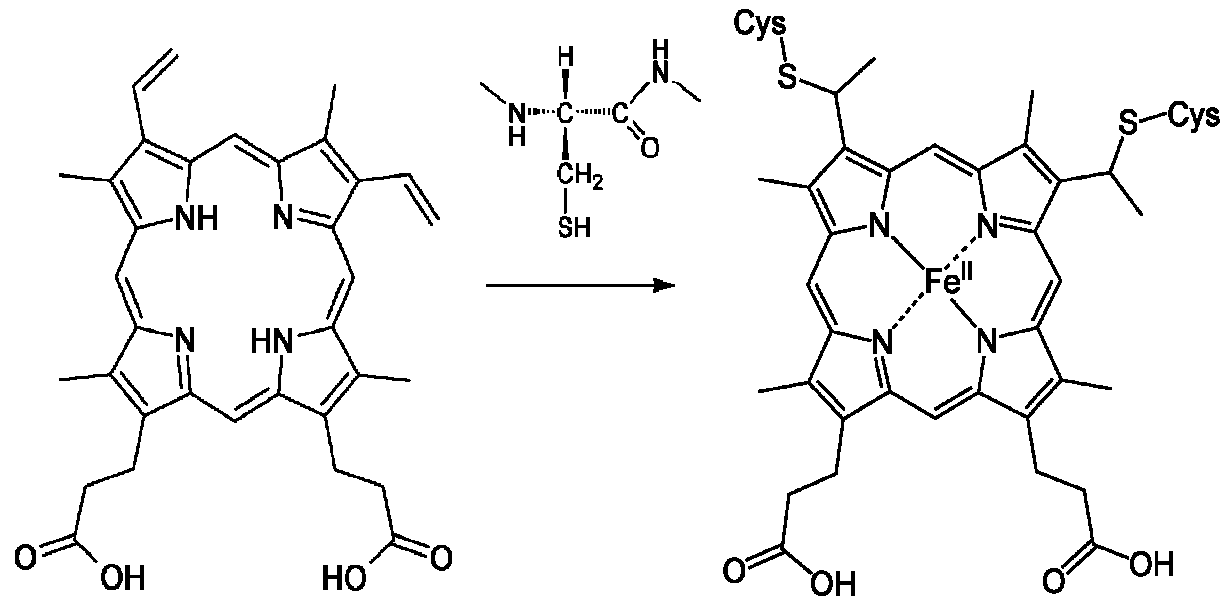


O_h -Koordination am Eisen
 Fe^{2+} (low spin) \leftrightarrow Fe^{3+} (low spin)
geringfügige Strukturänderungen

etwa 50 Cytochrome bekannt
Cytochrom a: positives Redoxpotenzial
Cytochrom b: 2x Histidin-Koordination

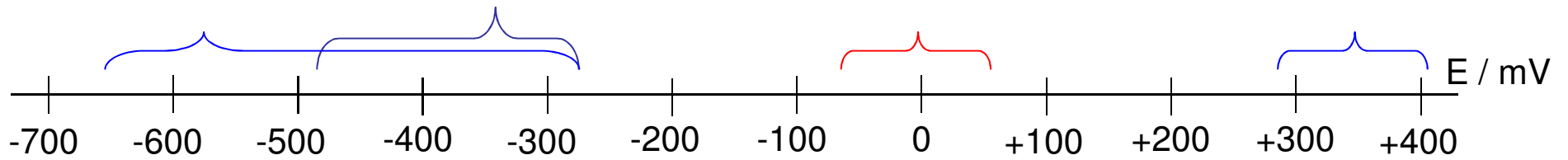
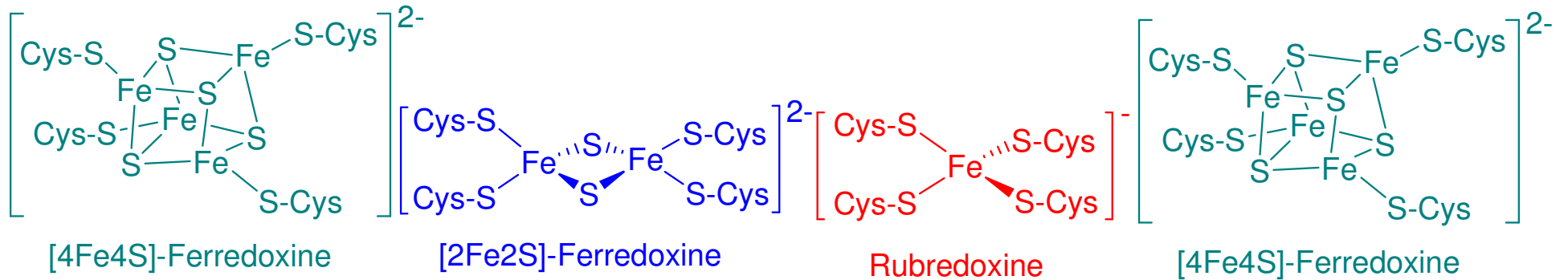
Elektronentransfer: Cytochrome

Kovalente Verankerung des Porphyrins im Protein



Addition
der zwei Vinylgruppen des Protoporphyrins IX
an zwei Cystein-Gruppen

Elektronentransport: Ferredoxine



$2Fe(II)/2Fe(III)$
 $S=0$
 ein Mößbauer-Signal

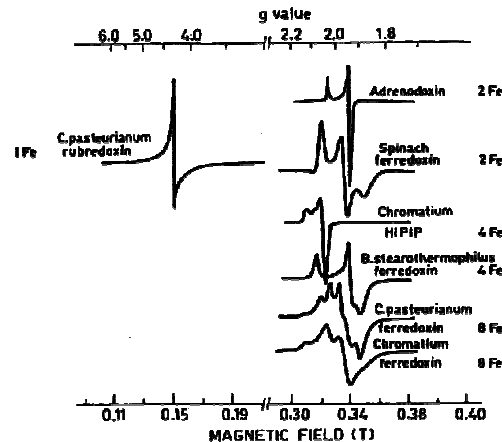
$Fe(III)/Fe(III)$
 high spin
 aber $S=0$

$Fe(II)/Fe(III)$
 beide high spin

$2Fe(II)/2Fe(III)$
 $S=0$

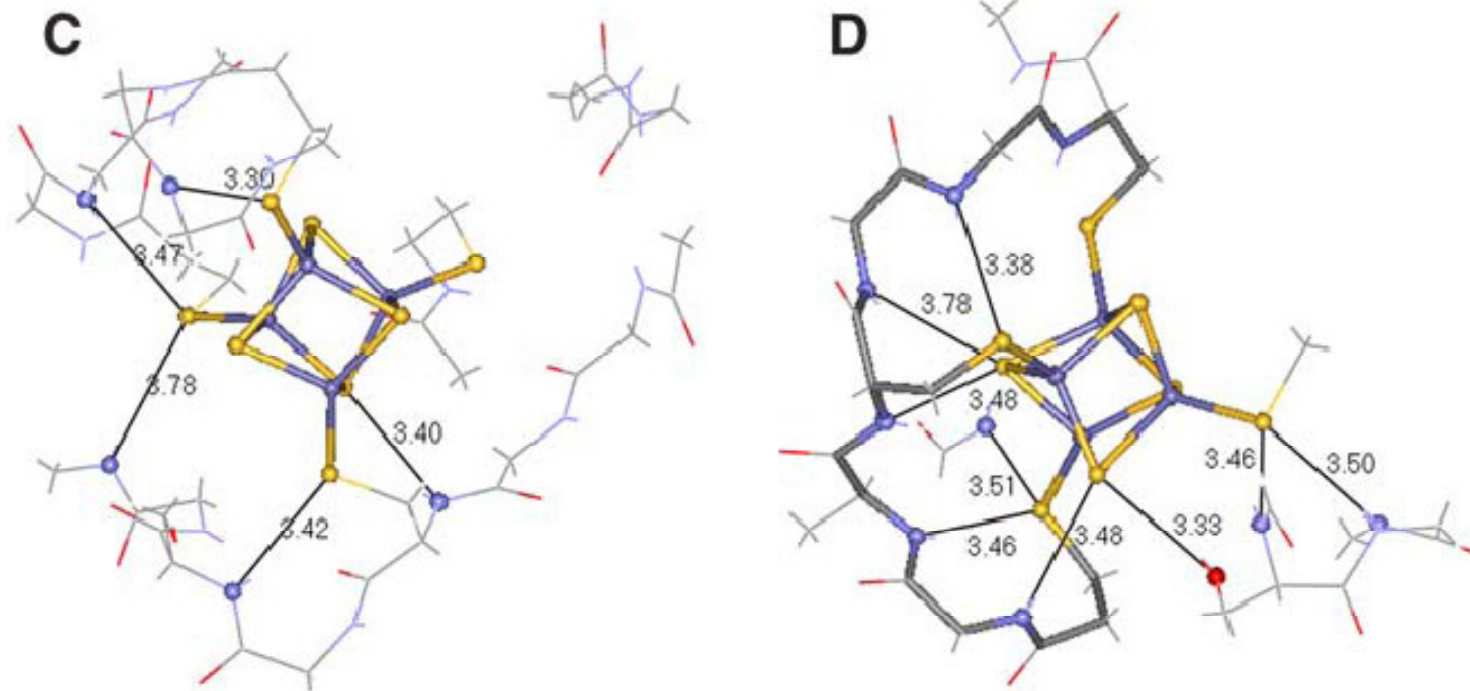
$3Fe(II)/1Fe(III)$
 $S=1/2$
 ein Mößbauer-Signal
 delokalisiert

$Fe(II)/Fe(III)$
 $S=1/2$
 zwei Mößbauer-Signale
 lokalisiert



$1Fe(II)/3Fe(III)$
 $S=1/2$

Regulation des Redoxpotenzials



Wasserstoff-Brückenbindungen zur Peptidkette

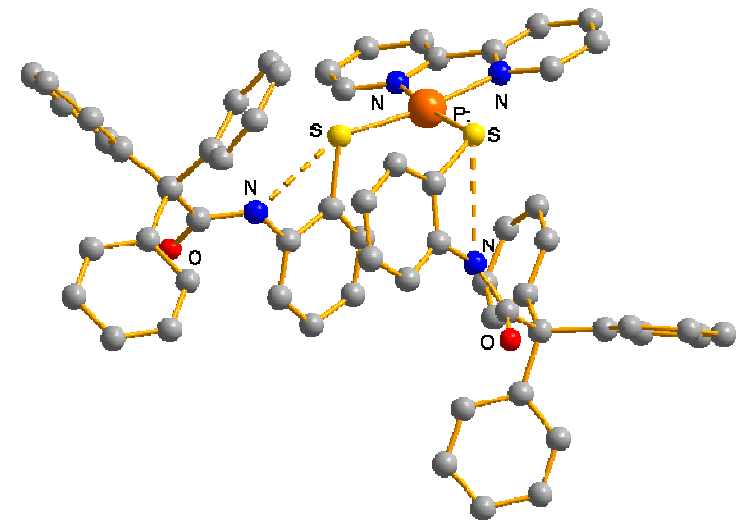
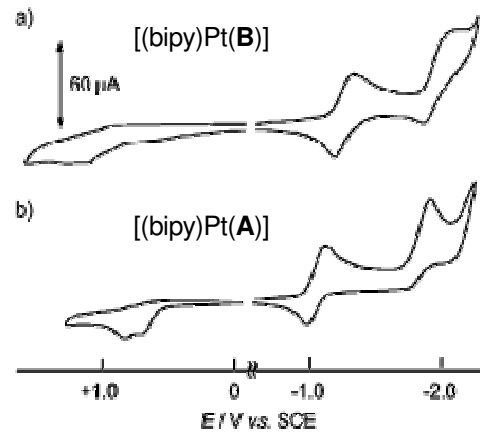
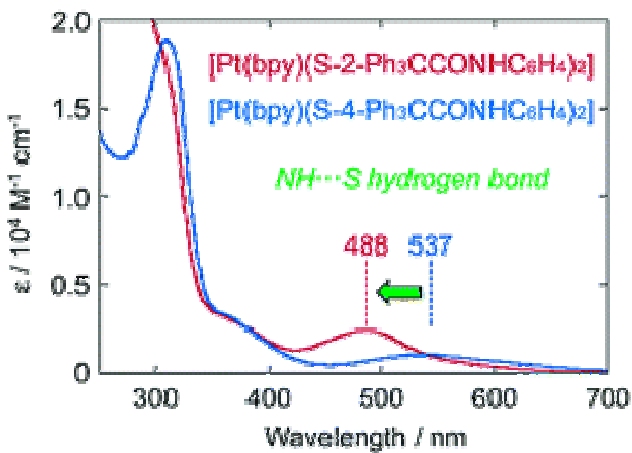
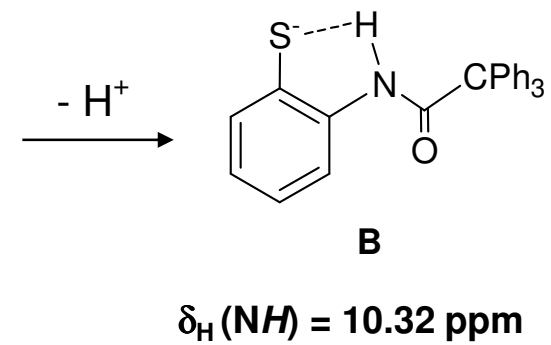
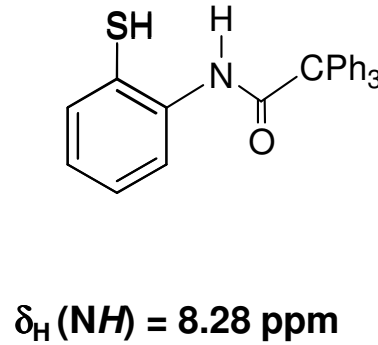
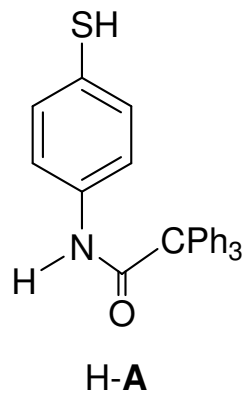
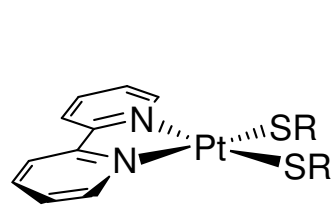
HiPIP: High Potential Iron Protein

Fd: Ferrdoxin

5

8

Regulation des Redoxpotenzials



$\delta_{\text{H}}(\text{NH}) = 8.74 \text{ ppm}$