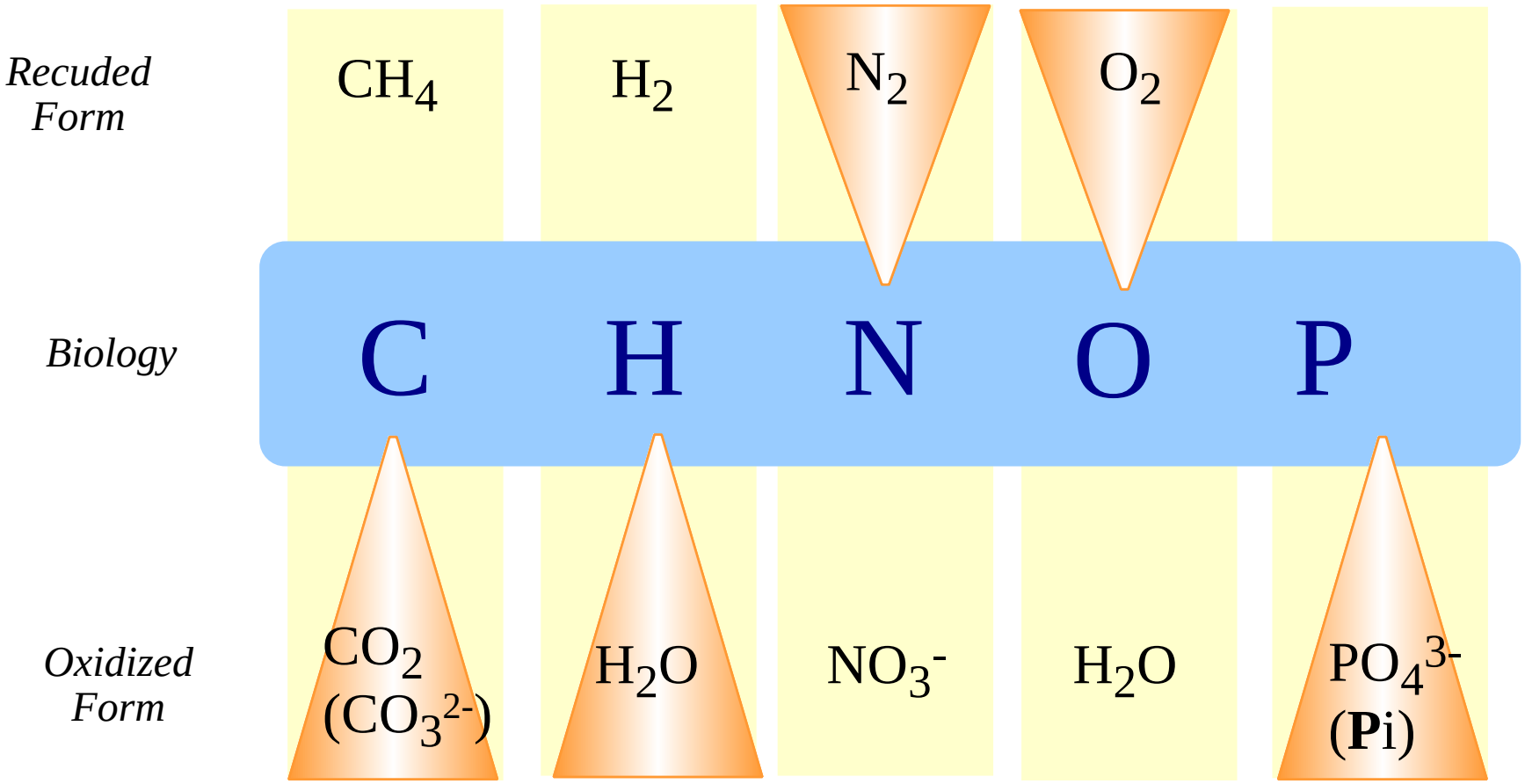
Nitrogenase Fixing Dinitrogen

- Metal Clusters in Biology -

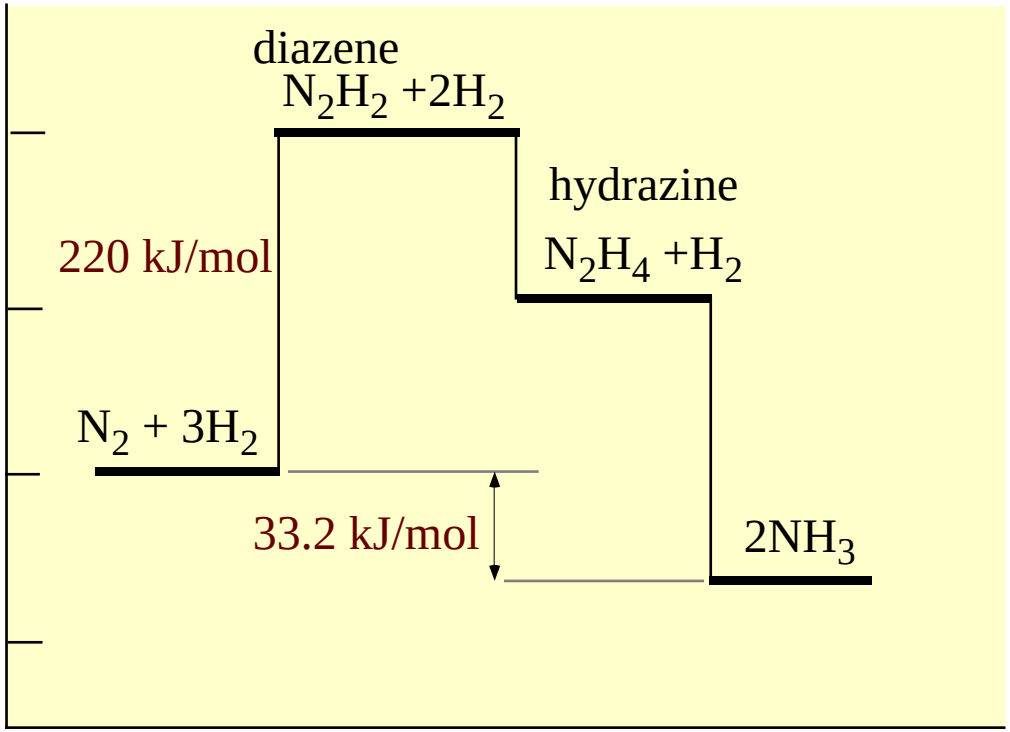
Main Elements in Biology



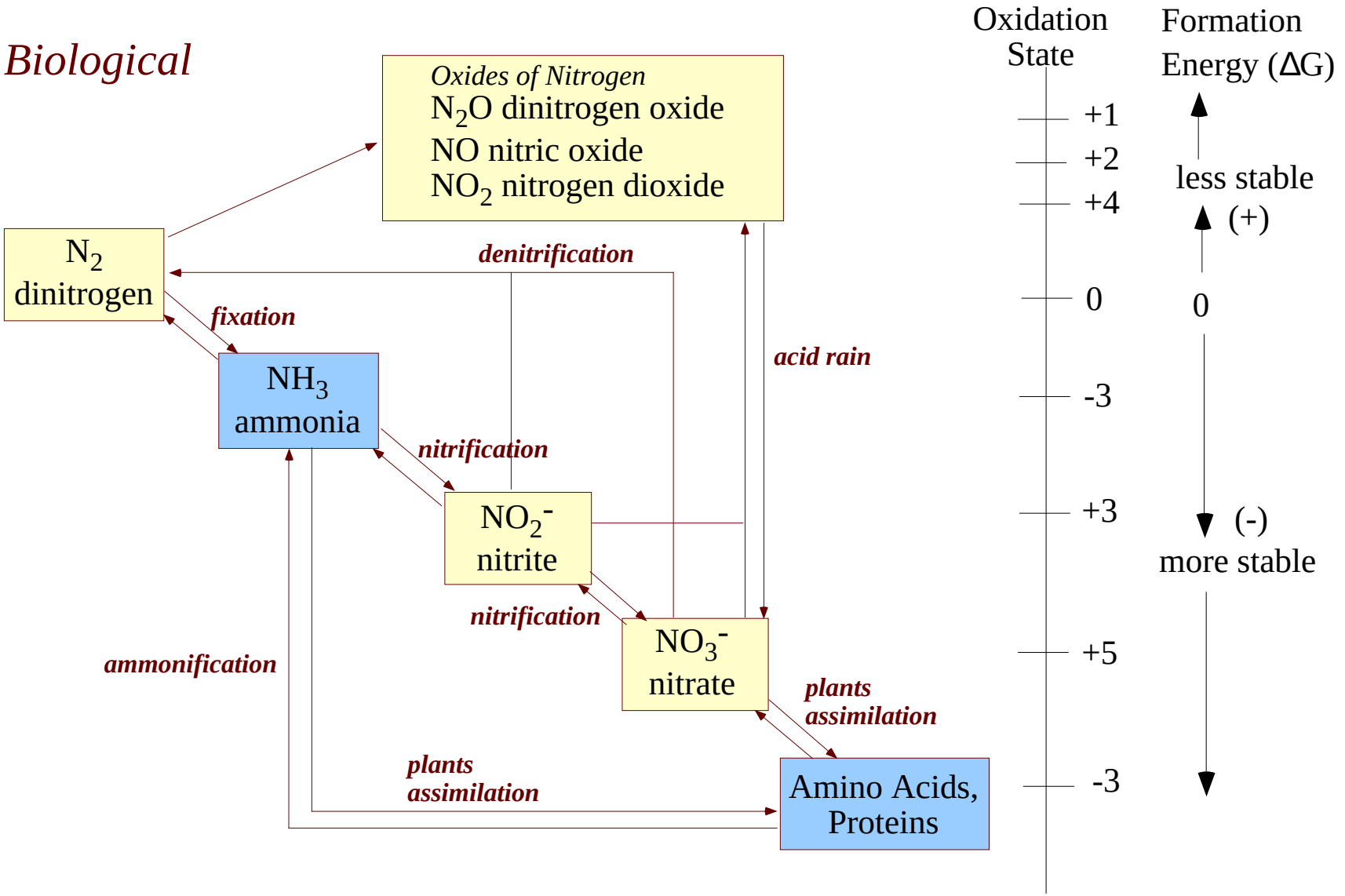
Reduction of Dinitrogen into Ammonia

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta G^0 = -33.2 \text{ kJ/mol}$$

Haber-Bosch process: cat. Fe_3O_4/sa Al_2O_3, 200-1000 atm, 200-500 °C

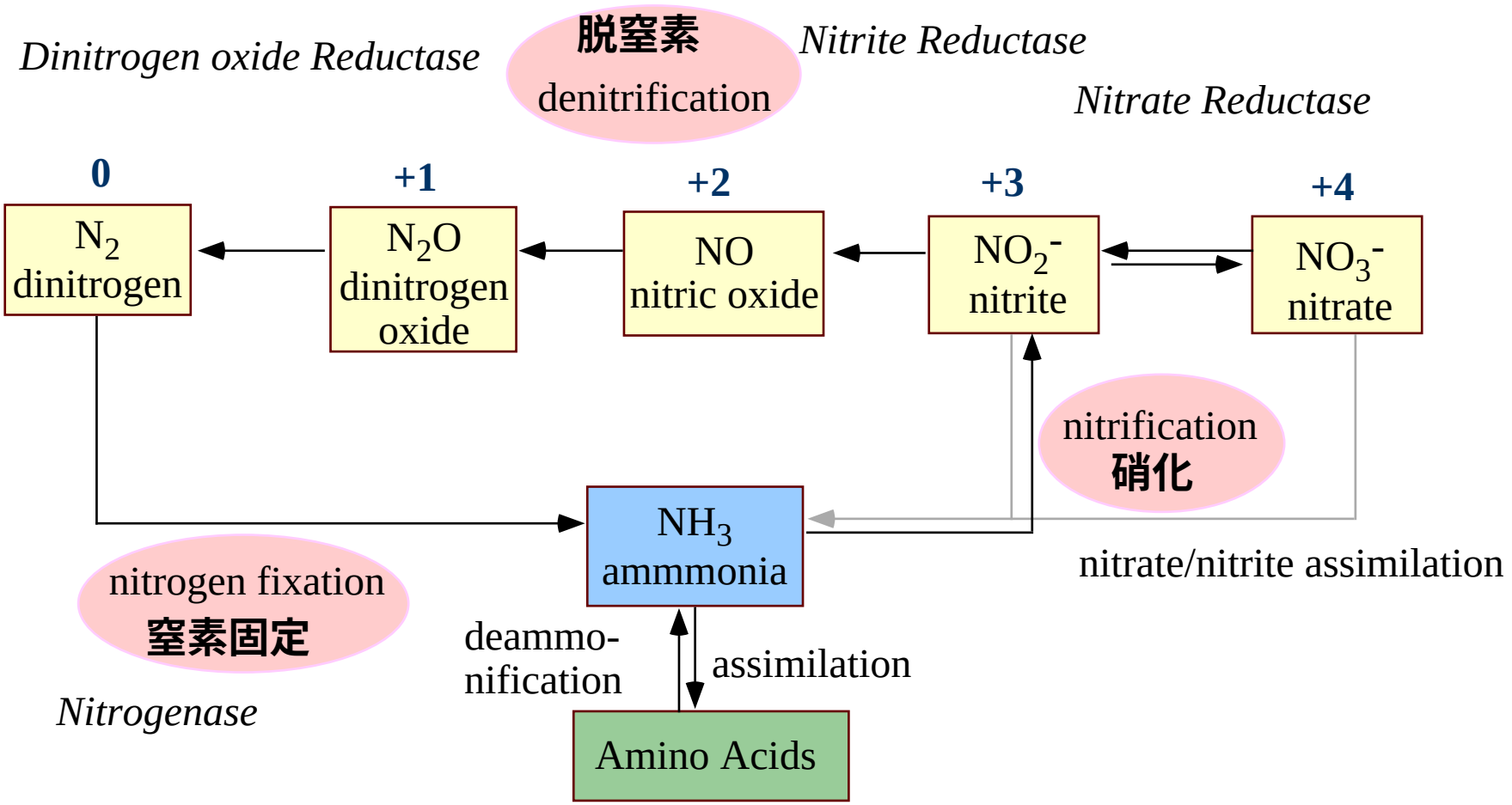


Chemical Forms and Cycle of Nitrogen

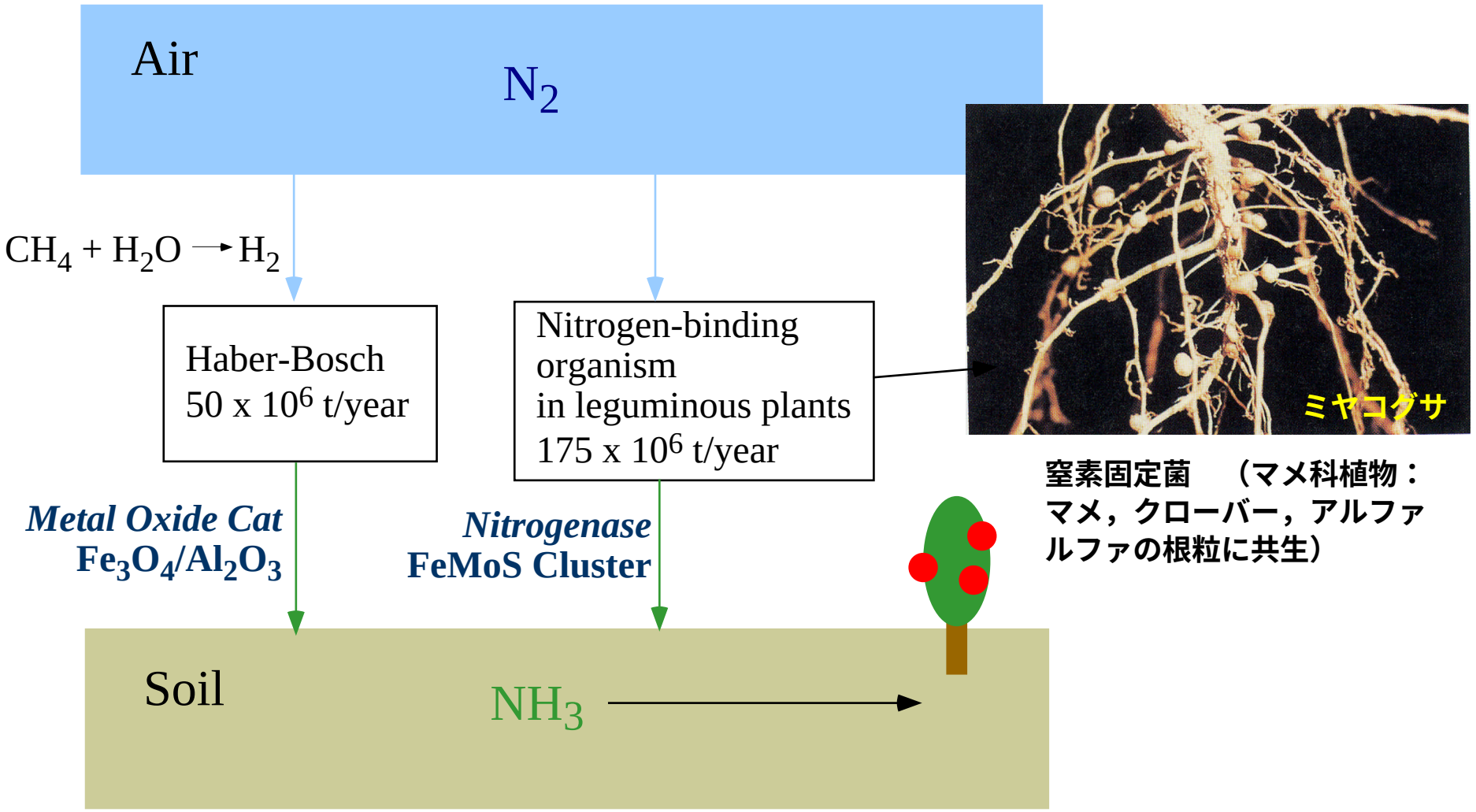


P. O'Neill, '*Environmetal Chemistry*', George, Allen, and Unwin, London, 1985

Biological Nitrogen Cycle



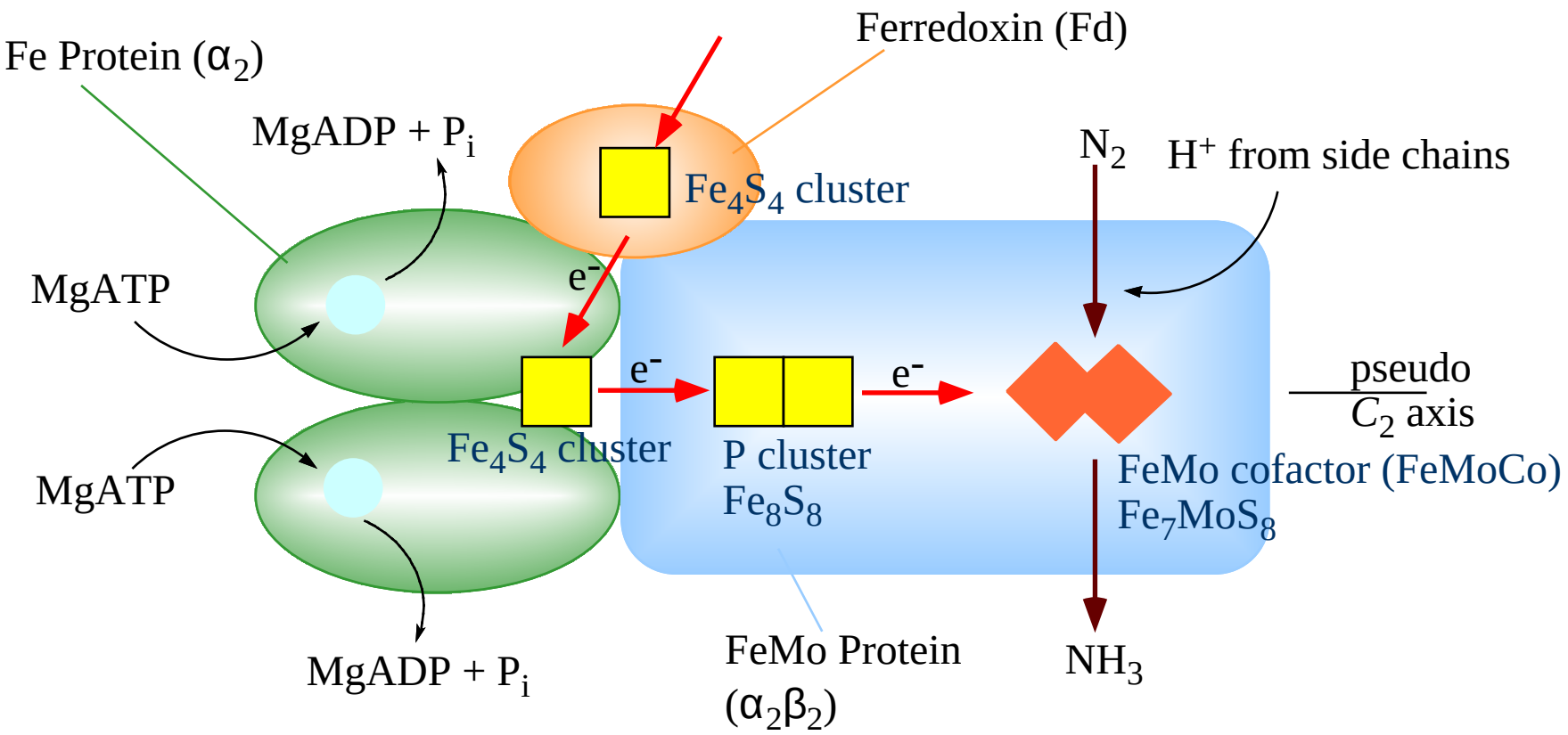
Nitrogen Fixation from Air



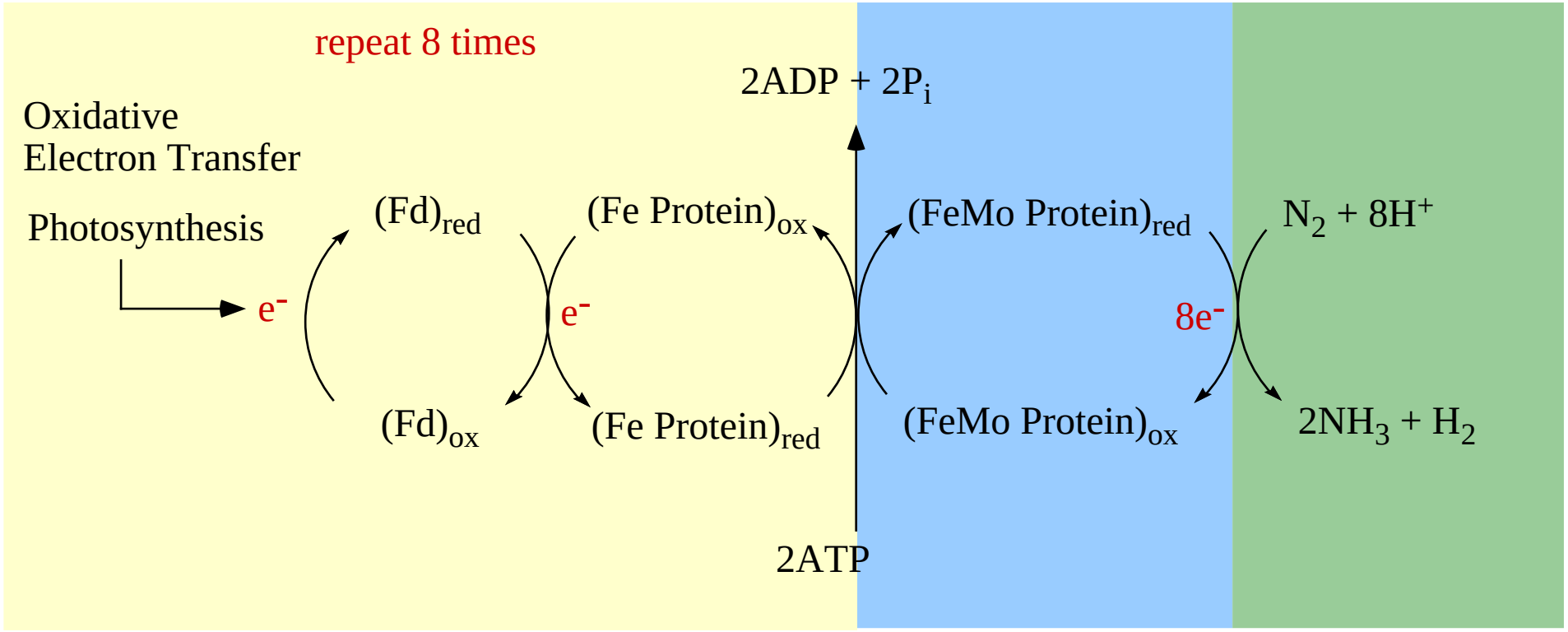
Nitrogenase Complex

$$N_2 + 8H^+ + 8e^- + 16MgATP \longrightarrow 2NH_3 + H_2 + 16MgADP + 16P_i$$

$\Delta G^0 = -65.6$ kJ/mol



Electron Shuttles in Nitrogenase



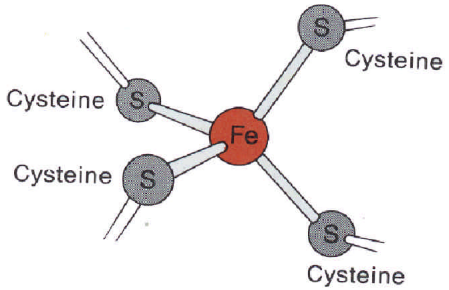
Ferredoxin (Fd)
Fe_4S_4 cluster

Fe Protein
Fe_4S_4 cluster

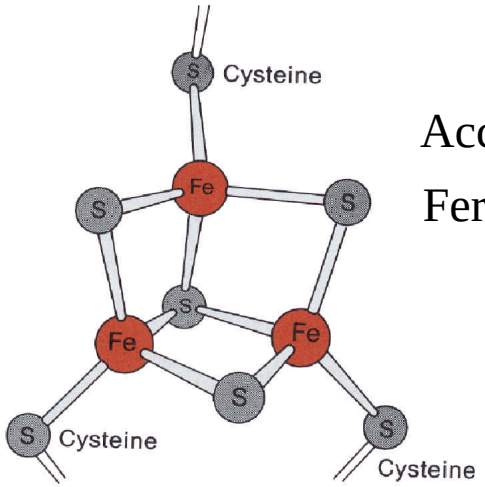
FeMo Protein
P cluster, Fe_8S_8
FeMo cofactor (FeMoCo), Fe_7MoS_8

Iron-Sulfur Clusters

Fe_nS_n: One Electron Transfer Proteins

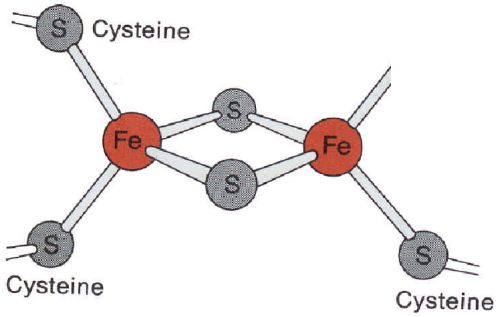


Rubredoxin [1Fe-0S]

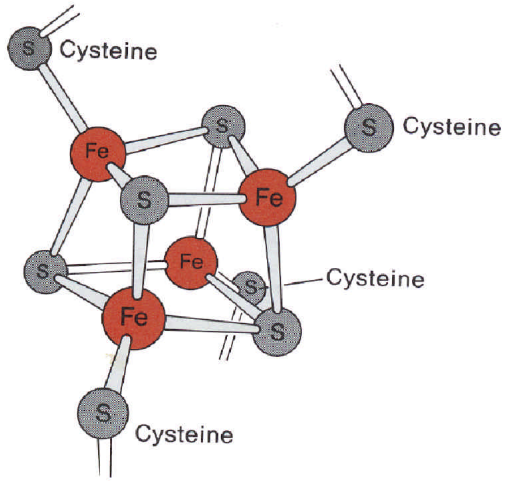


Acconitase [3Fe-3S]

Ferredoxin [3Fe-4S]



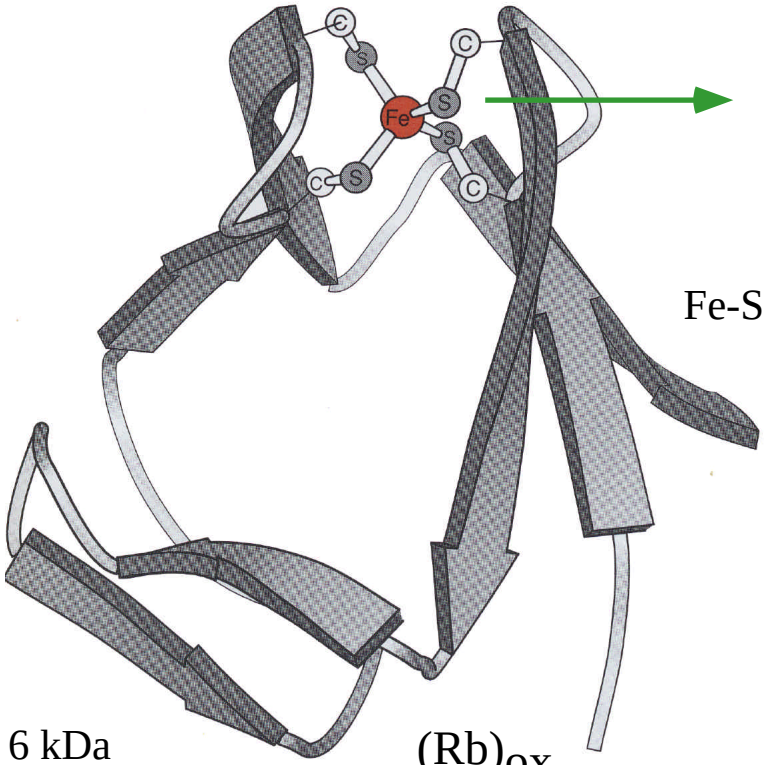
Ferredoxin [2Fe-2S]



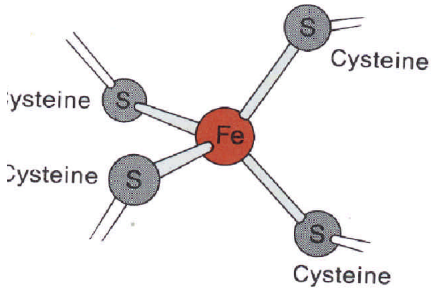
Ferredoxin [4Fe-4S]

Rubredoxin (Rb)

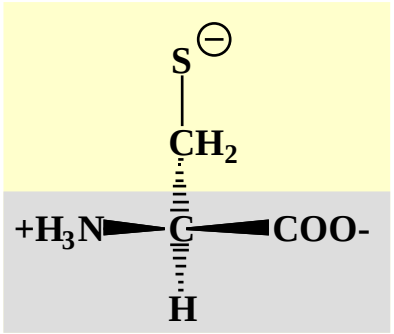
Cys_{39}-X-X-Cys_{42}-Gly Cys_6-X-X-Cys_9-Gly



6 kDa $(Rb)_{ox}$



Fe-S = av. 2.29(2) Å Td



Cys (C) pKa 8.35

$(Rb)_{ox}$ Fe(III) d^5 high spin

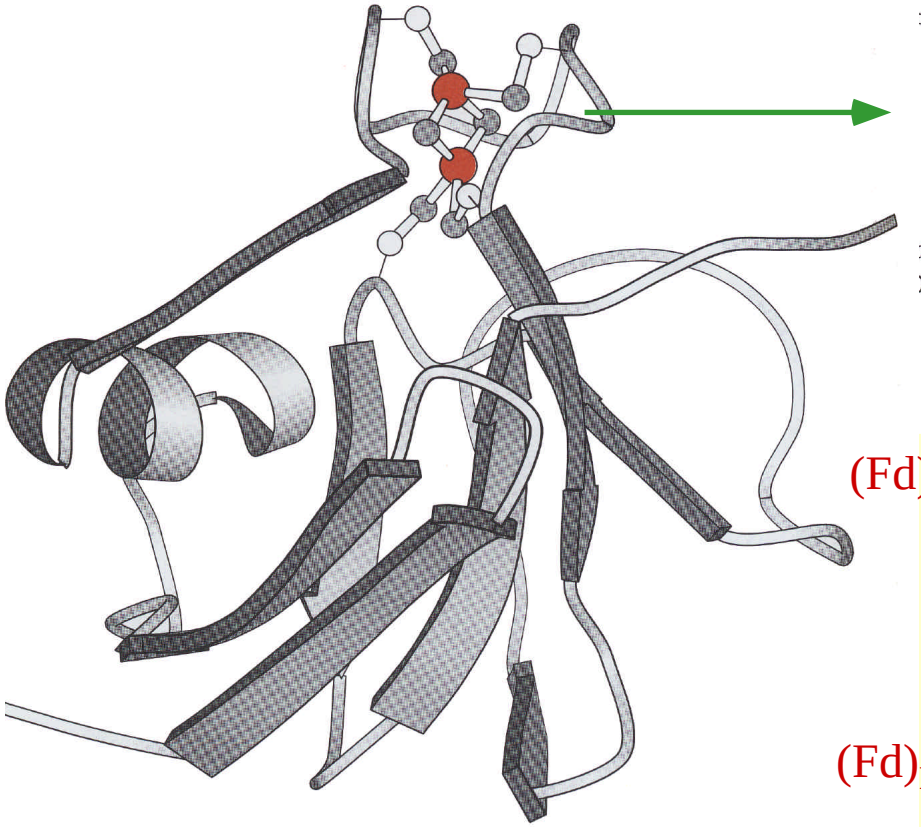
$-e^-$ ⇕ e^- $E_{1/2}$ = -50~+50 mV (pH 7)

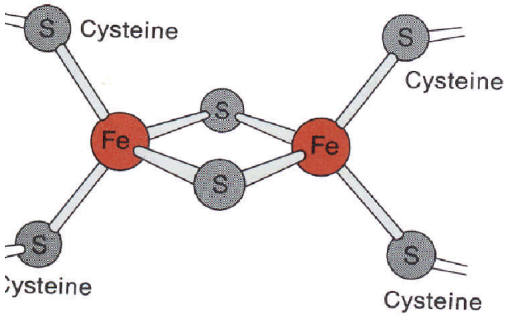
$(Rb)_{red}$ Fe(II) d^6 low spin

C. pasteuriabun Rubredoxin
bacteria

Ferredoxin [2Fe-2S]

-CXXXXCXXC-X_{29}-C-





Fe···Fe = 2.7 Å

$(Fd)_{ox}$ Fe(III)Fe(III) (-2) high spin

$-e^-$ e^- $E_{1/2}$ = -300~-400 mV

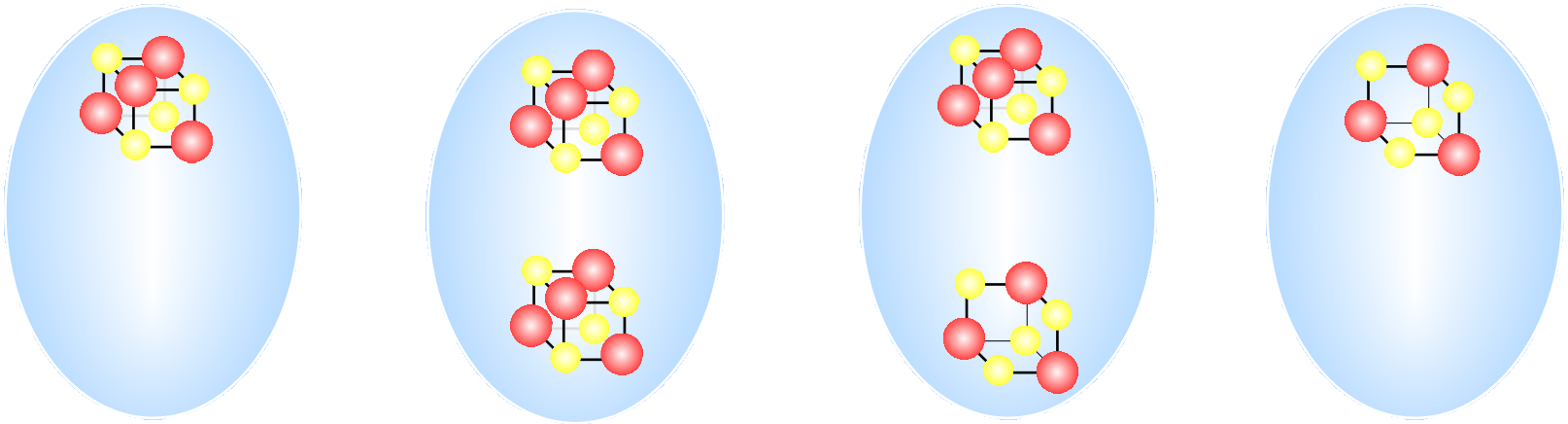
$(Fd)_{red}$ Fe(II)Fe(III) (-3) high spin

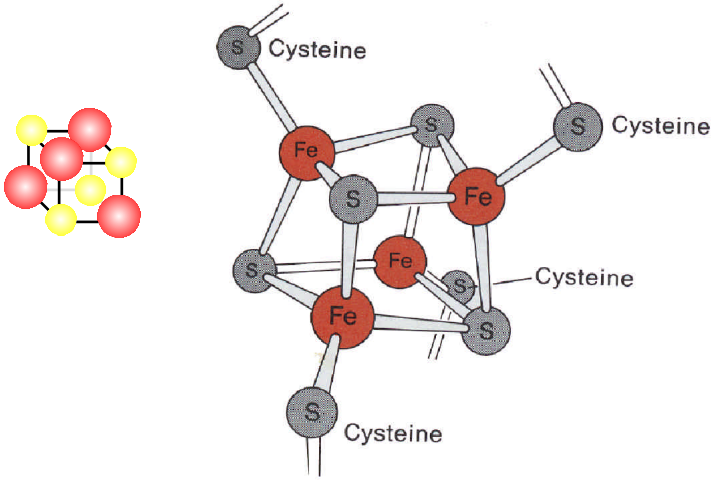
S. platenis Ferredoixn (Fd)

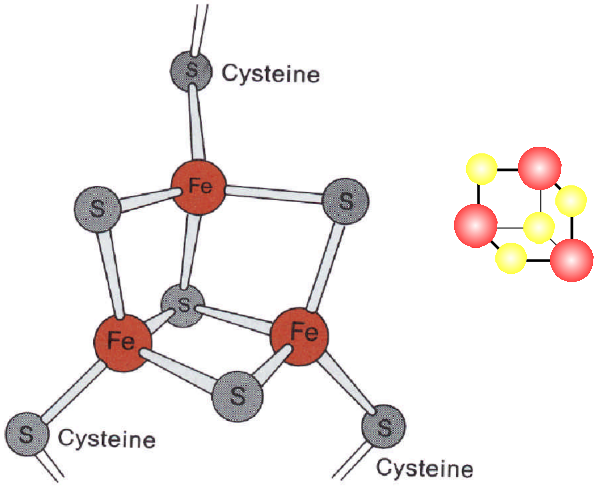
11 kDa

Classification of Ferredoxins [4Fe-4S], [3Fe-4S]

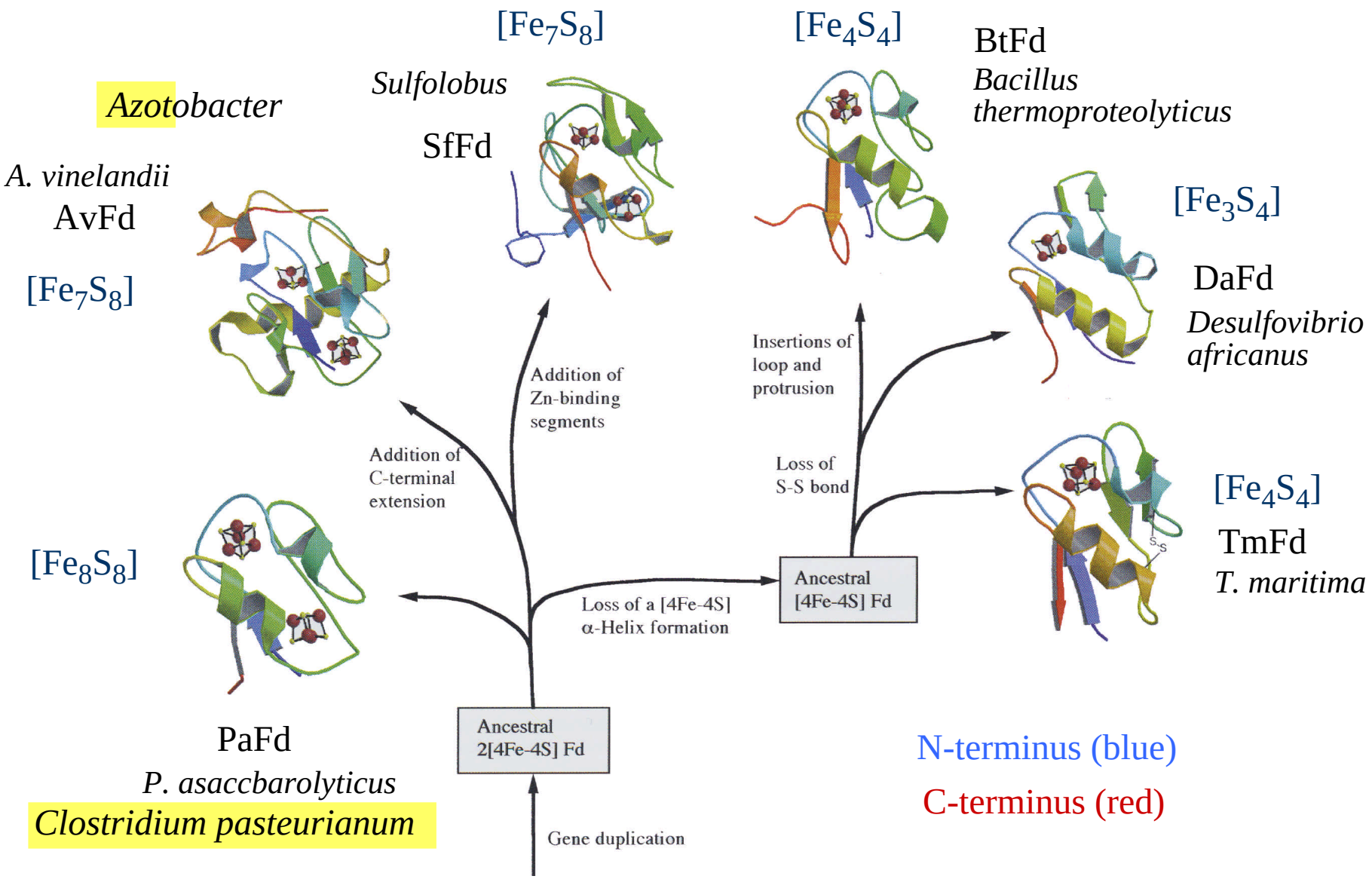
[4Fe-4S] 2[4Fe-4S] [4Fe-4S][3Fe-4S] [3Fe-4S]



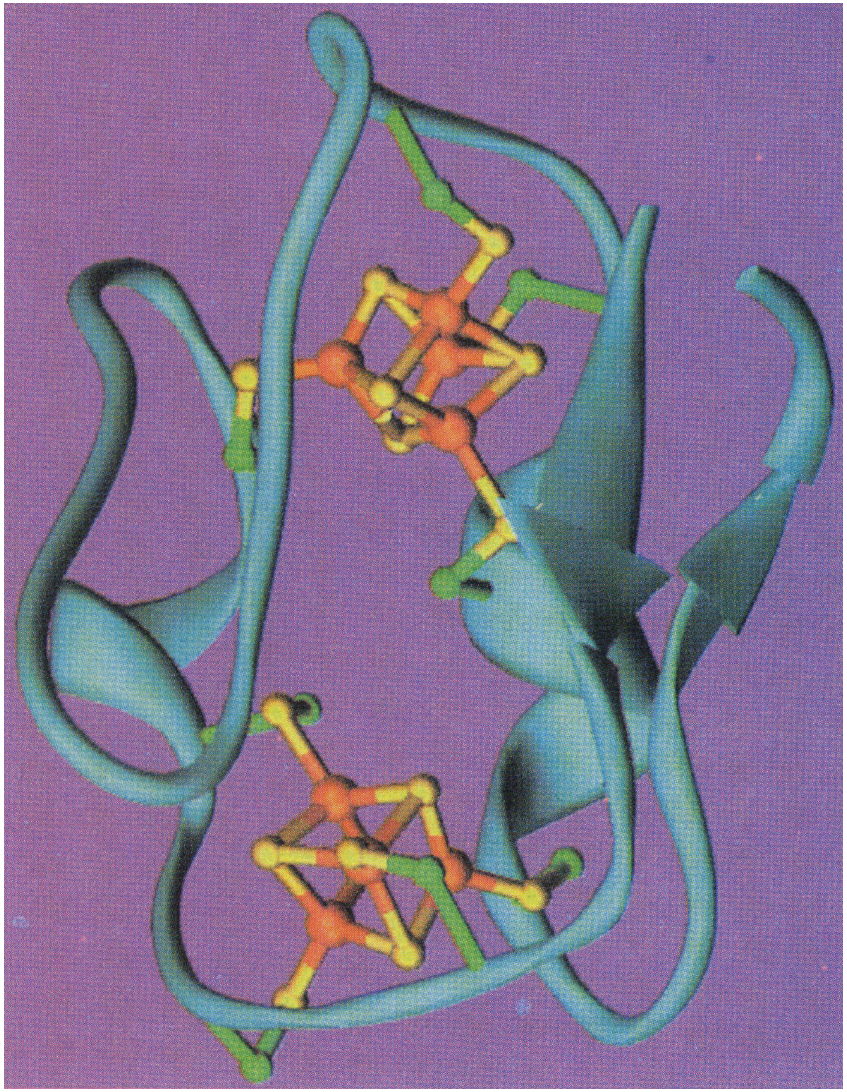




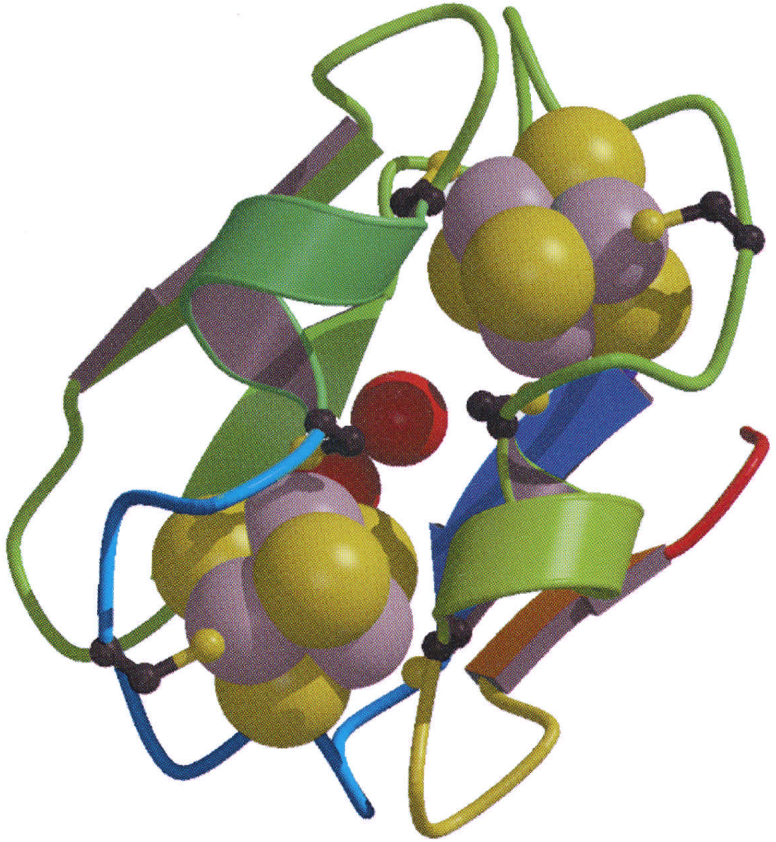
Probable Evolutionary Process of Bacterial Ferredoxins



X-ray Crystal Structures of Ferredoxin from *P. asaccbarolyticus* (PaFd)



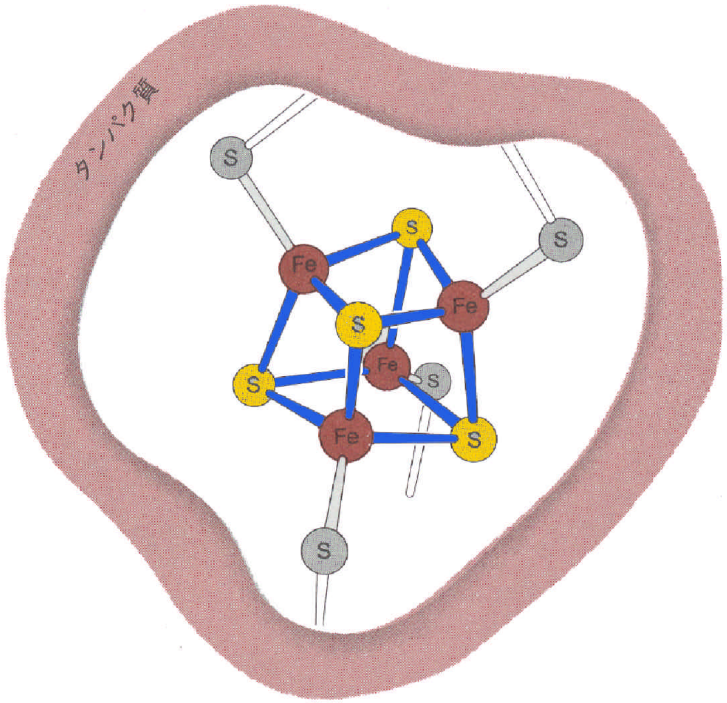
The most ancestral and popular type of Fds with 2 x [4Fe-4S] clusters.

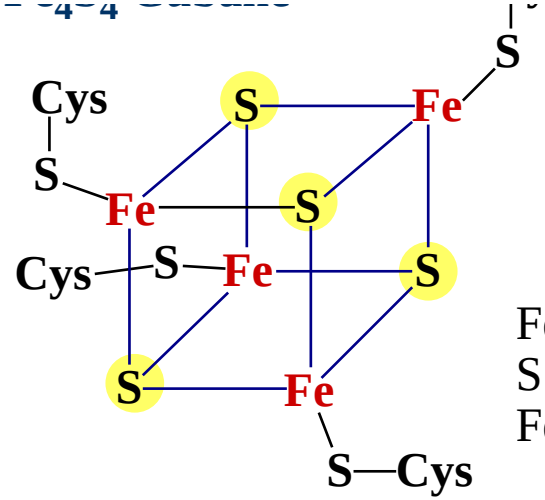


CaFd
Clostridium pasteurianum
窒素固定菌（嫌気性細菌）

-$XC_8XXC_{11}XXC_{14}XXXC_{18}$-⋯-$XC_{35}XXC_{38}XXC_{41}XXXC_{45}$-

Structure and Property of [4Fe-4S] Core





Fe···Fe = 2.75 Å
S···S = 3.55 Å
Fe-S = 2.30 Å

super Ox form $[Fe(II)Fe(III)_3S_4(SR)_4]^-$

$\{Fe(II)Fe(III)_3S_4\}^{3+}$

$-e^-$ ⇕ e^- +50 mV

Ox form $[Fe(II)_2Fe(III)_2S_4(SR)_4]^{2-}$

$\{Fe(II)_2Fe(III)_2S_4\}^{2+}$

$-e^-$ ⇕ e^- -400 mV

Red form $[Fe(II)_3Fe(III)S_4(SR)_4]^{3-}$

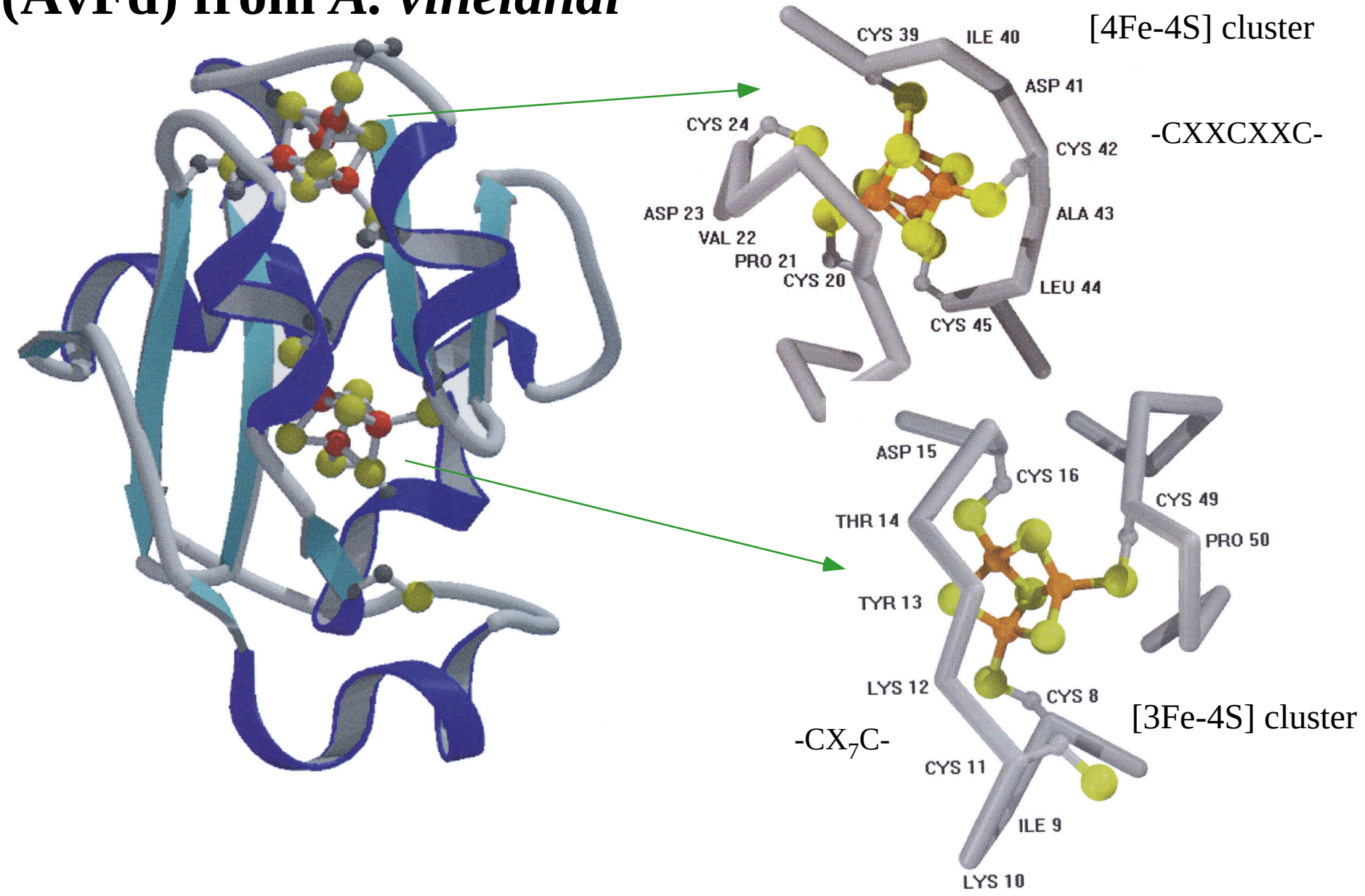
$\{Fe(II)_3Fe(III)S_4\}^{+}$

(CaFd)

↓

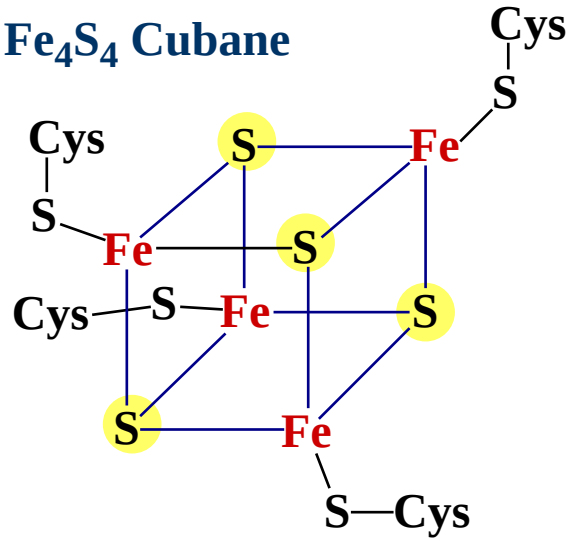
One Electron Transfer

X-ray Crystal Structures of Azotobacter Ferredoxin (AvFd) from *A. vinelandii*



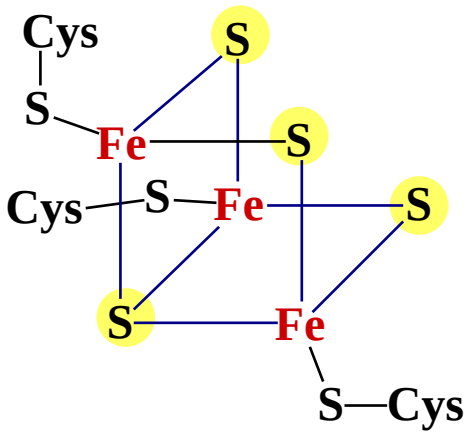
Structures and Properties of [4Fe-4S] and [3Fe-4S] Cores of AvFd

Fe_4S_4 Cubane



Fe^{n+} ⇌ $-Fe^{n+}$

Fe_3S_4 Incomplete Cubane



Ox form	$[Fe(II)_2Fe(III)_2S_4(SR)_4]^{2-}$	$[Fe(III)_3S_4(SR)_4]^{3-}$
	$\{Fe(II)_2Fe(III)_2S_4\}^{2+}$	$\{Fe(III)_3S_4\}^{+}$
	$-e^-$ ⇕ e^- -645 mV	$-e^-$ ⇕ e^- -446 mV
Red form	$[Fe(II)_3Fe(III)S_4(SR)_4]^{3-}$	$[Fe(II)Fe(III)_2S_4(SR)_4]^{4-}$
	$\{Fe(II)_3Fe(III)S_4\}^{+}$	$\{Fe(II)Fe(III)_2S_4\}^{0}$

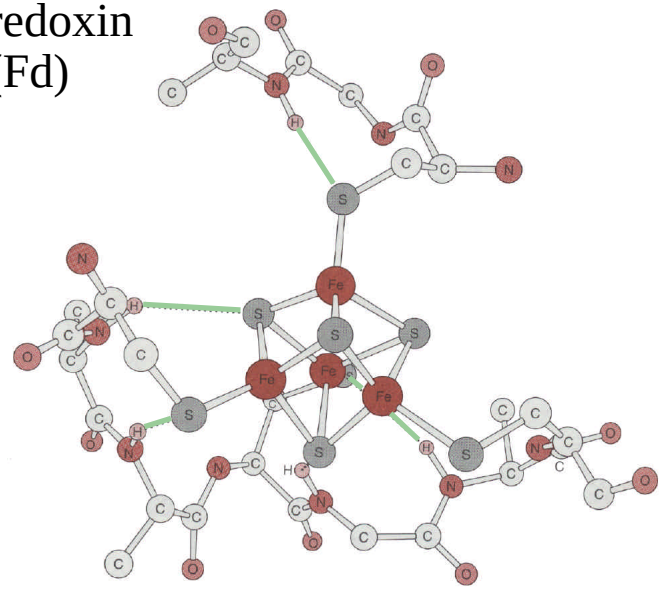
Redox Potentials of Iron-Sulfur Proteins

protein	typical origin	type of Fe/S center	E (mV)
Rd	*Clostridium pasteurianum*	$[Fe]^{3+/2+}$	-60
2Fe Fd	*spinach*	$[Fe_2S_2]^{2+/1+}$	-420
Rieske center	*adrenal mitochondria*	$[Fe_2S_2]^{2+/1+}$	+280
4Fe Fd	*Bacillus stearothermophilus*	$[Fe_4S_4]^{2+/1+}$	-280
8Fe Fd	*Clostridium pasteurianum*	$[Fe_4S_4]^{2+/1+}$	-400
Fd II	*D. gigas*	$[Fe_3S_4]^{1+/0}$	-130
Fd I	*Azotovacter vinelandii*	$[Fe_3S_4]^{1+/0}$ $[Fe_4S_4]^{2+/1+}$	-450 -650
HiPIP	*Chromatium vinosum*	$[Fe_4S_4]^{2+/3+}$	+350

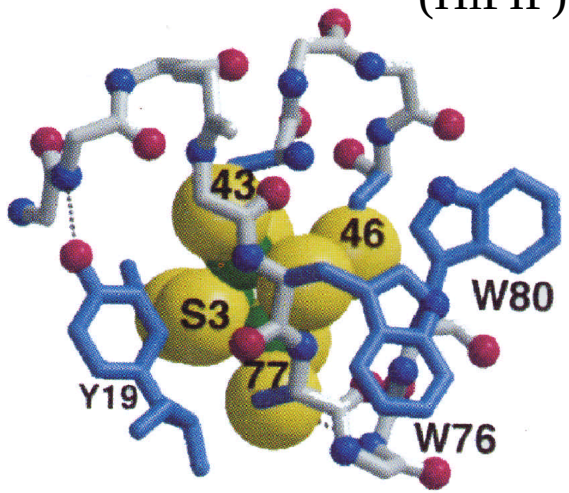
Rd = rubredoxin, Fd = ferredoxin, HiPIP = high potential iron-sulfur protein

Hydrophobicity and Hydrogen Bonding Effects on [4Fe-4S] Centers

Ferredoxin
(Fd)



High Potential Iron Protein
(HiPIP)



super oxidized Fd

+50 mV $-e^-$ e^-

oxidized Fd

-400 mV $-e^-$ e^-

reduced Fd

Clostridium pasteurianum

$\{Fe(II)Fe(III)_3S_4\}^{3+}$
(-1)

$\{Fe(II)_2Fe(III)_2S_4\}^{2+}$
(-2)

$\{Fe(II)_3Fe(III)S_4\}^{+}$
(-3)

oxidized HiPIP

$-e^-$ e^- +350 mV

reduced HiPIP

$-e^-$ e^- -600 mV

super reduced HiPIP

Chromatium vinosum

Synthetic Model Compounds

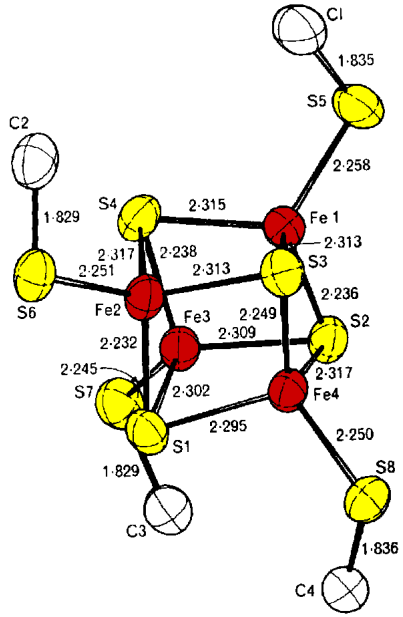
Spontaneous Self-Assembly ~1980 R. H. Holm (USA)

$FeCl_3$ + RSH (NaHS, NaOMe)

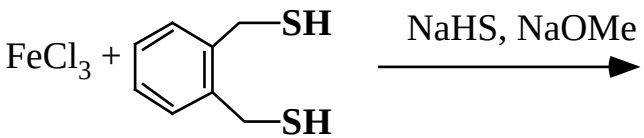
$[Fe_2S_2(CO)_4]$ + RSSR + RS^- → **$[Fe_4S_4(SR)_4]^{2-}$**

FeS + RSSR + RS^-

$[Fe_4S_4(SR)_4]^{2-}$ —ArSH→ **$[Fe_4S_4(SAr)_4]^{2-}$**

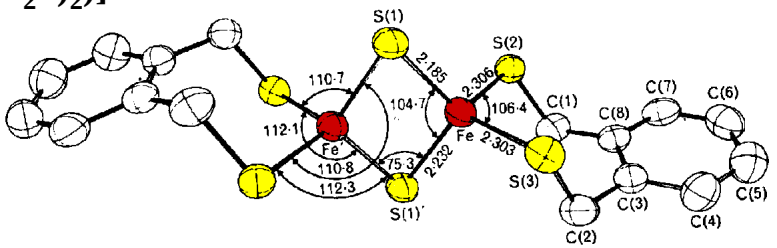


X-ray Structure of $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$



$FeCl_3$ + —NaHS, NaOMe→ **$[Fe_2S_2(o\text{-}C_6H_4(CH_2S)_2)]^{2-}$**

$[Fe_2S_2(o\text{-}C_6H_4(CH_2S)_2)]^{2-}$ —ArSH→ **$[Fe_2S_2(ArS)_2)]^{2-}$**



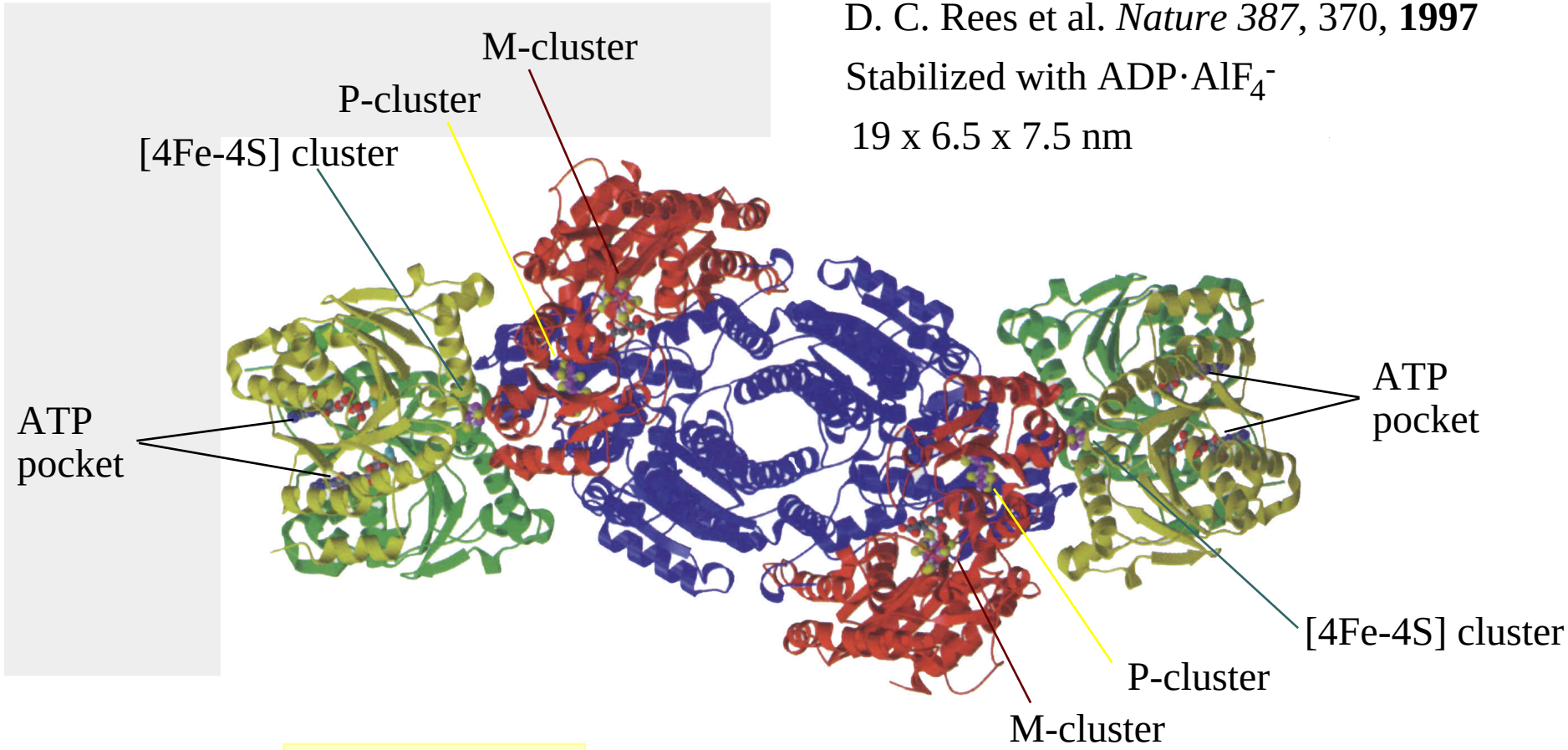
X-ray Structure of $(Et_4N)_2[Fe_2S_2(o\text{-}(SCH_2)_2Ph)_2]$

Azotobacter vinelandii Nitrogenase Complex

D. C. Rees et al. *Nature 387*, 370, **1997**

Stabilized with ADP·AlF_4^-

19 x 6.5 x 7.5 nm

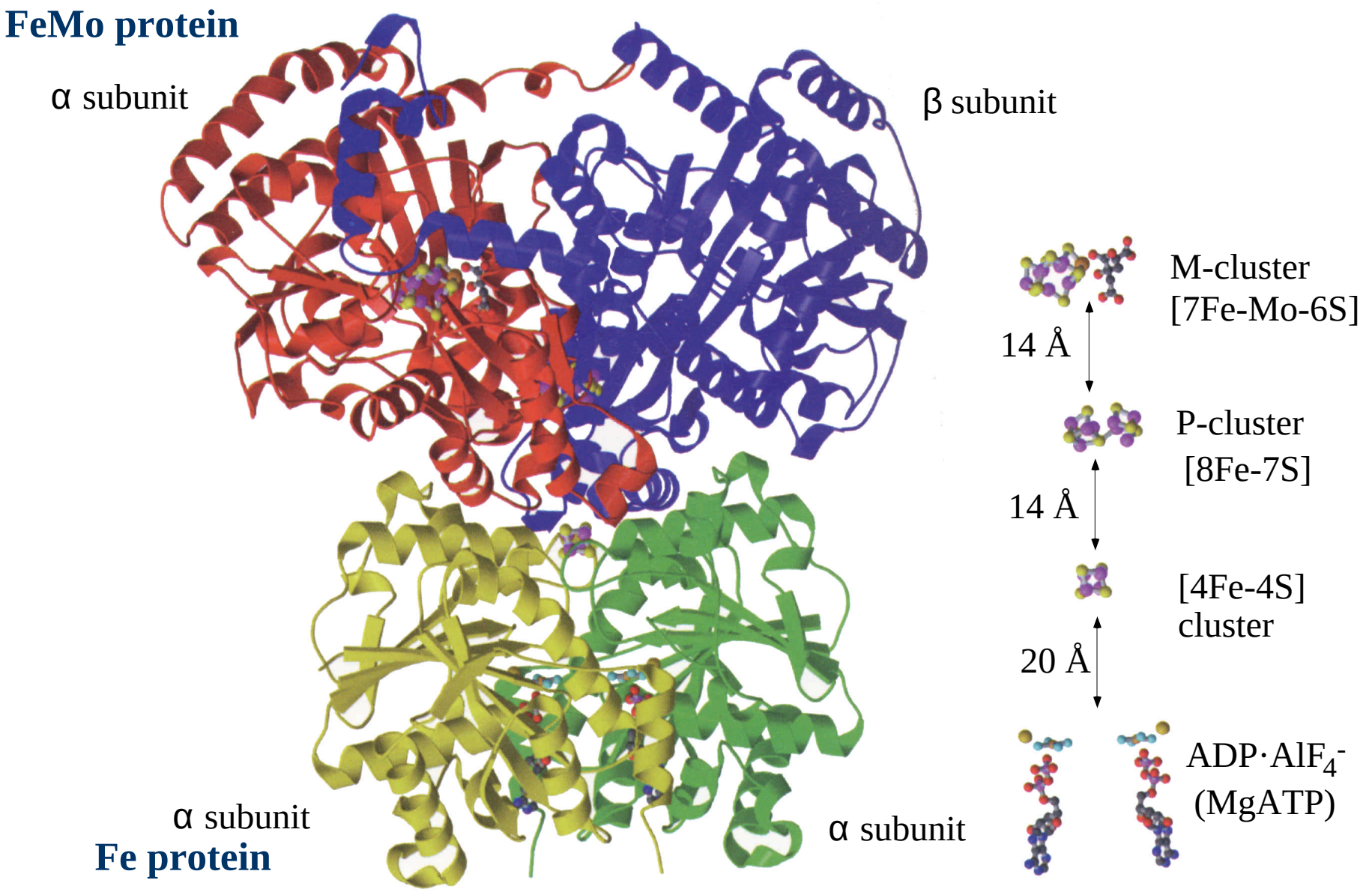


Fe protein
α_2 64 kD

FeMo protein
$\alpha_2\beta_2$ 220 kD

Fe protein
α_2 64 kD

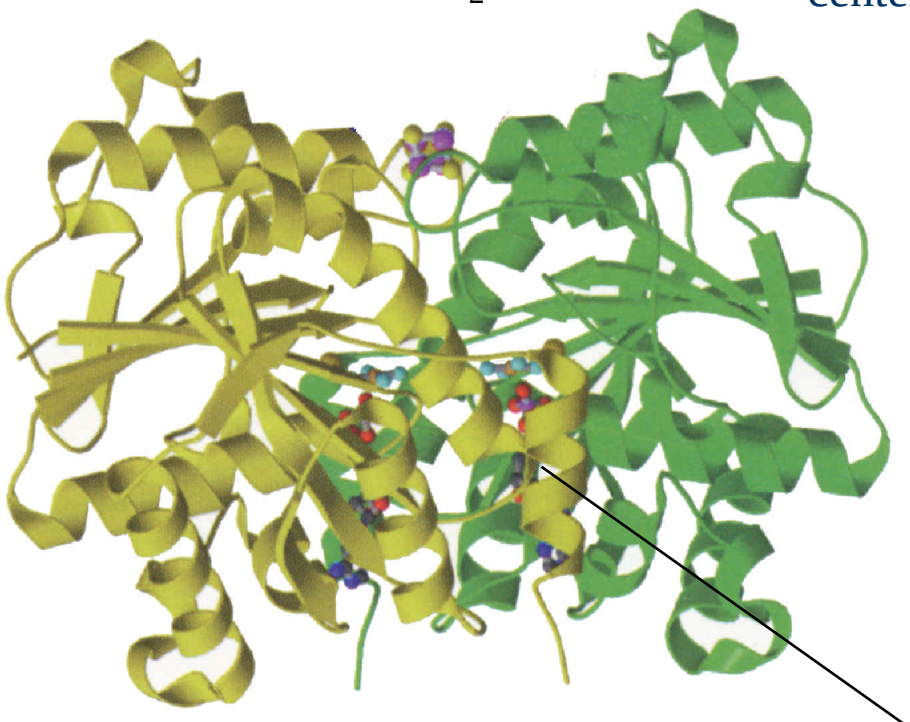
A Half Unit of *Av* Nitrogenase Complex

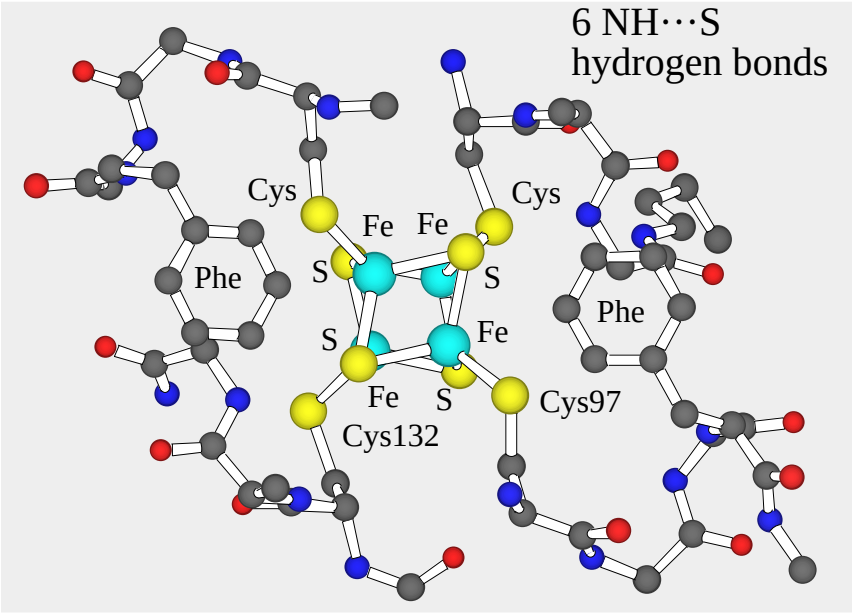


Structure of *Av* Fe protein

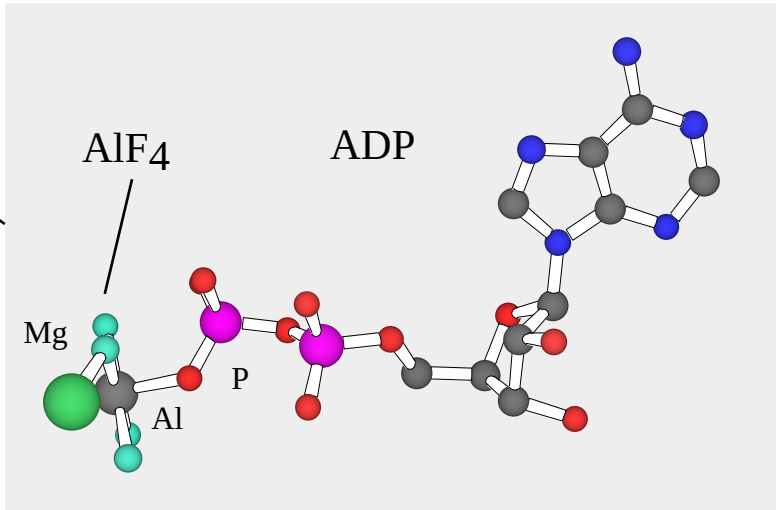
pseudo C_2 axis

[4Fe-4S] center





20 Å



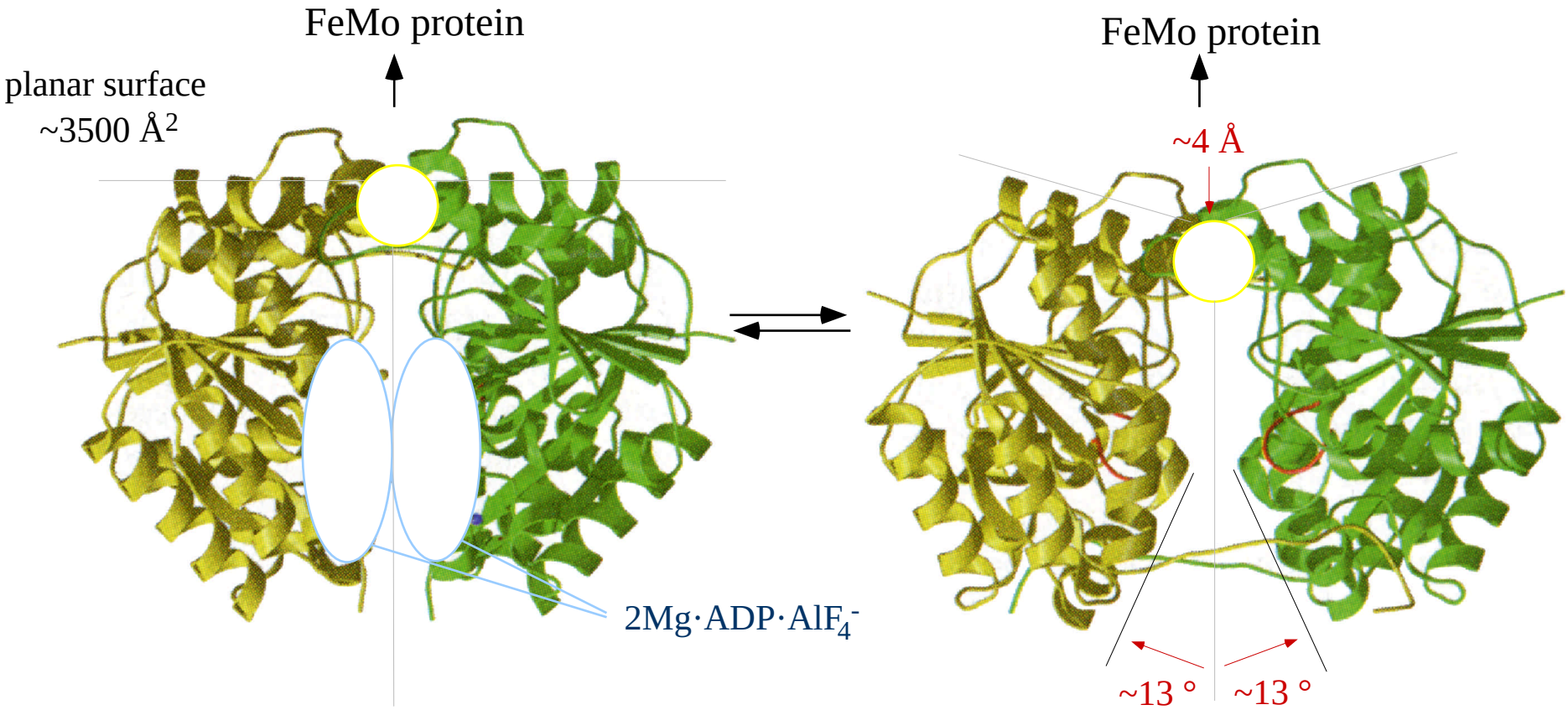
$\gamma(289aa)_2$

PDB code 1N2C

Iron butterfly

ATP pocket between α-helix of γ and γ'

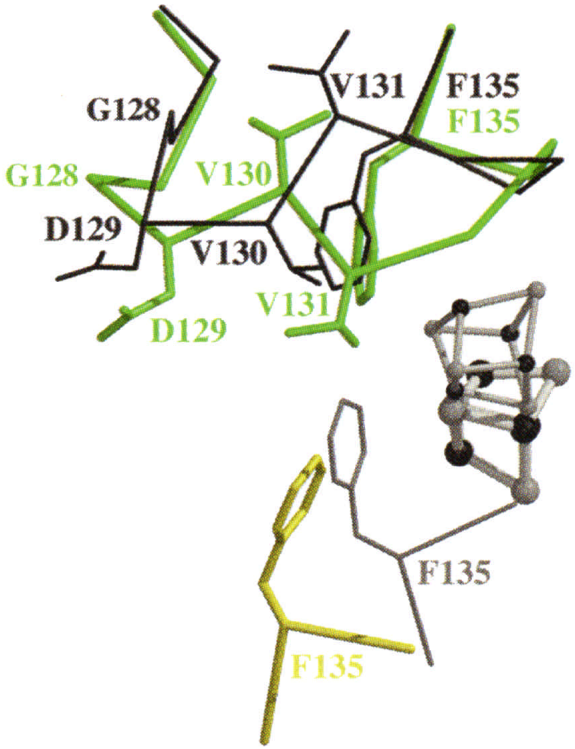
Structural Change of Av Fe Protein with Binding of Mg·ADP·AlF4-



ADP Binding
PDB 1N2C

ADP Unbinding
PDB 1MIN

Structural Change around the [4Fe-4S] Center of *Av* Fe Protein with Binding of $Mg \cdot ADP \cdot AlF_4^-$



Ox

$\{Fe^{II}_2Fe^{III}_2S_4(CysS)_4\}^{2-}$

$[Fe^{II}_2Fe^{III}_2S_4]^{2+}$

e^- Reduction Potential

Red

$\{Fe^{II}_3Fe^{III}S_4(CysS)_4\}^{3-}$

$[Fe^{II}_3Fe^{III}S_4]^{+}$

hydrophilic
(hydrogen bonds)
hydrohobic
(Phe135, Val130, 131)

\- **Unbinding** **Binding**

-620 mV

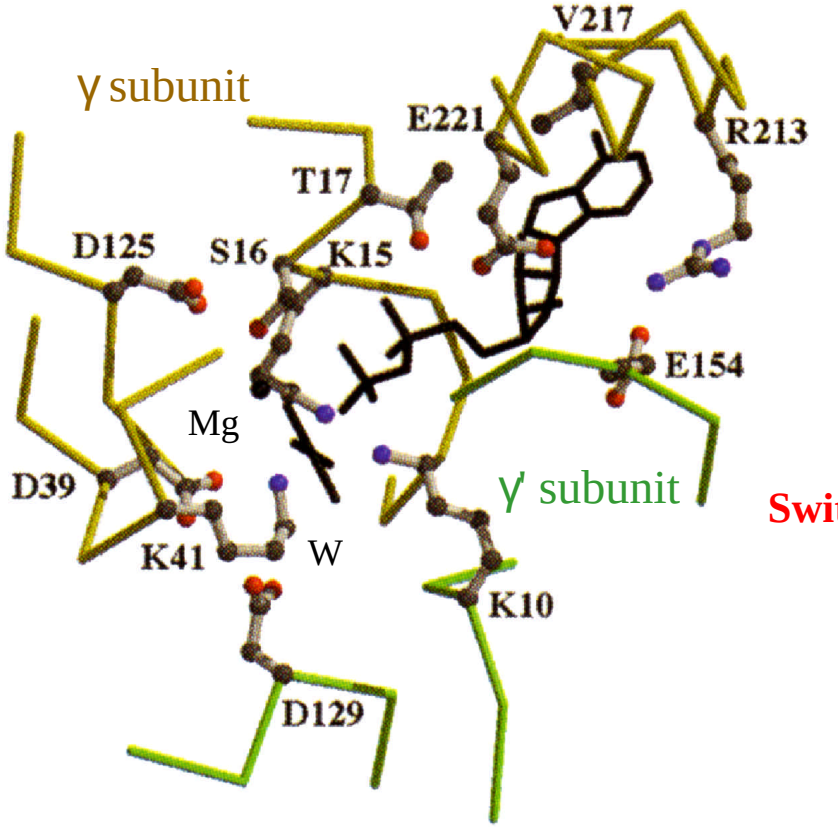
-300 mV

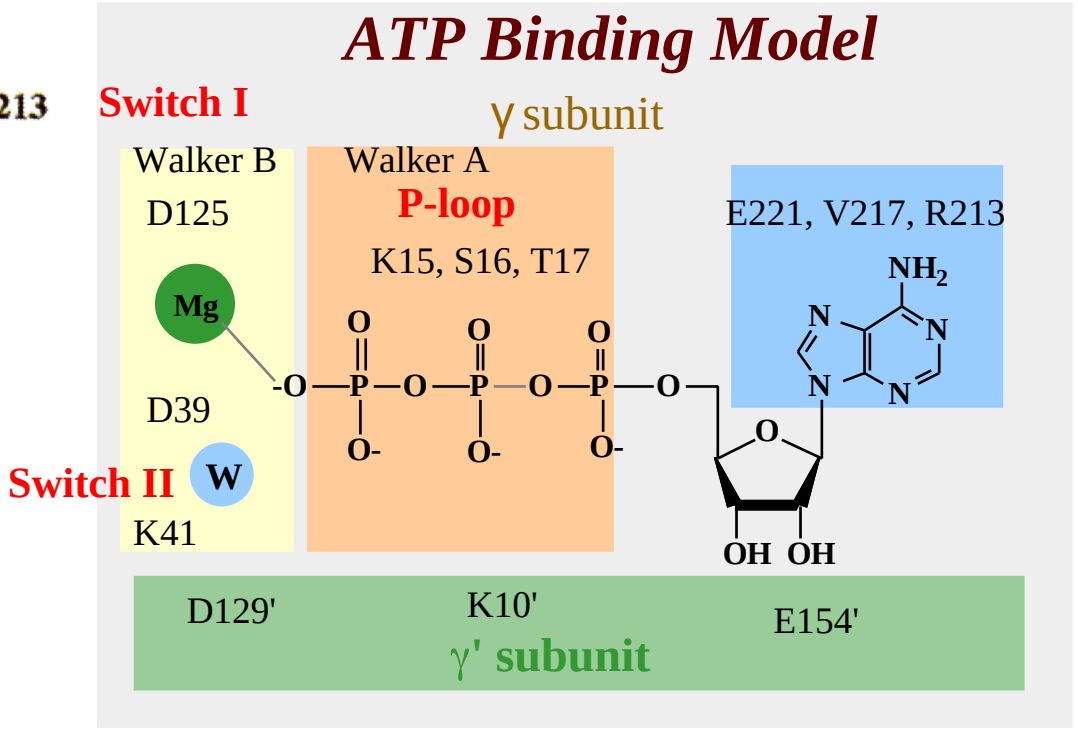
stabilized unstabilized
reduction form

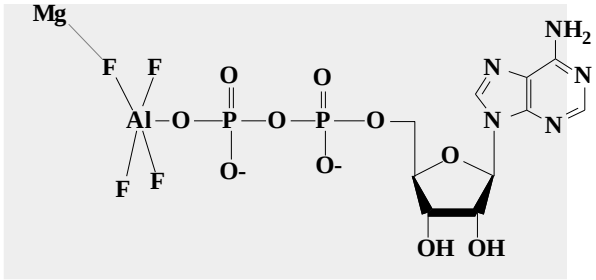
\+

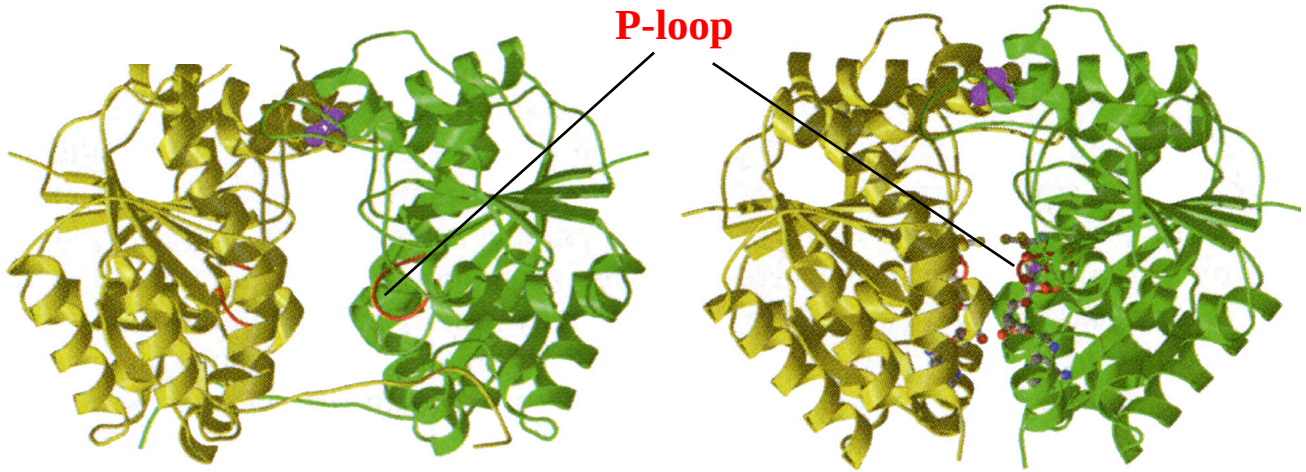
Thick green (γ subunit) and yellow (γ′ subunit) linesare for the complexed structure and thin black (γ subunit) and gray (γ′ subunit) lines for the uncomplexed structure.

Mg·ADP·AlF$_4^-$ (ATP) Binding Site

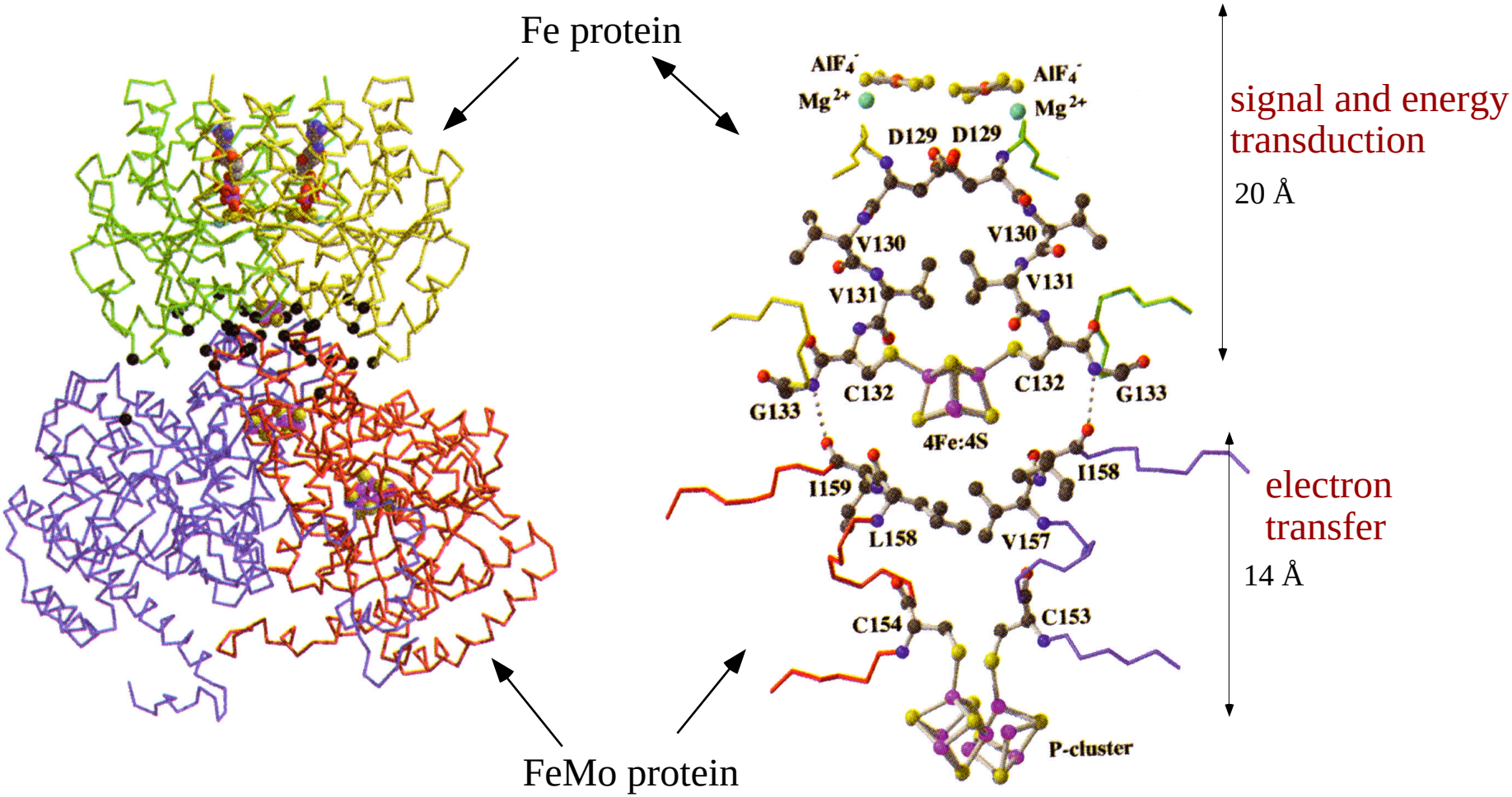








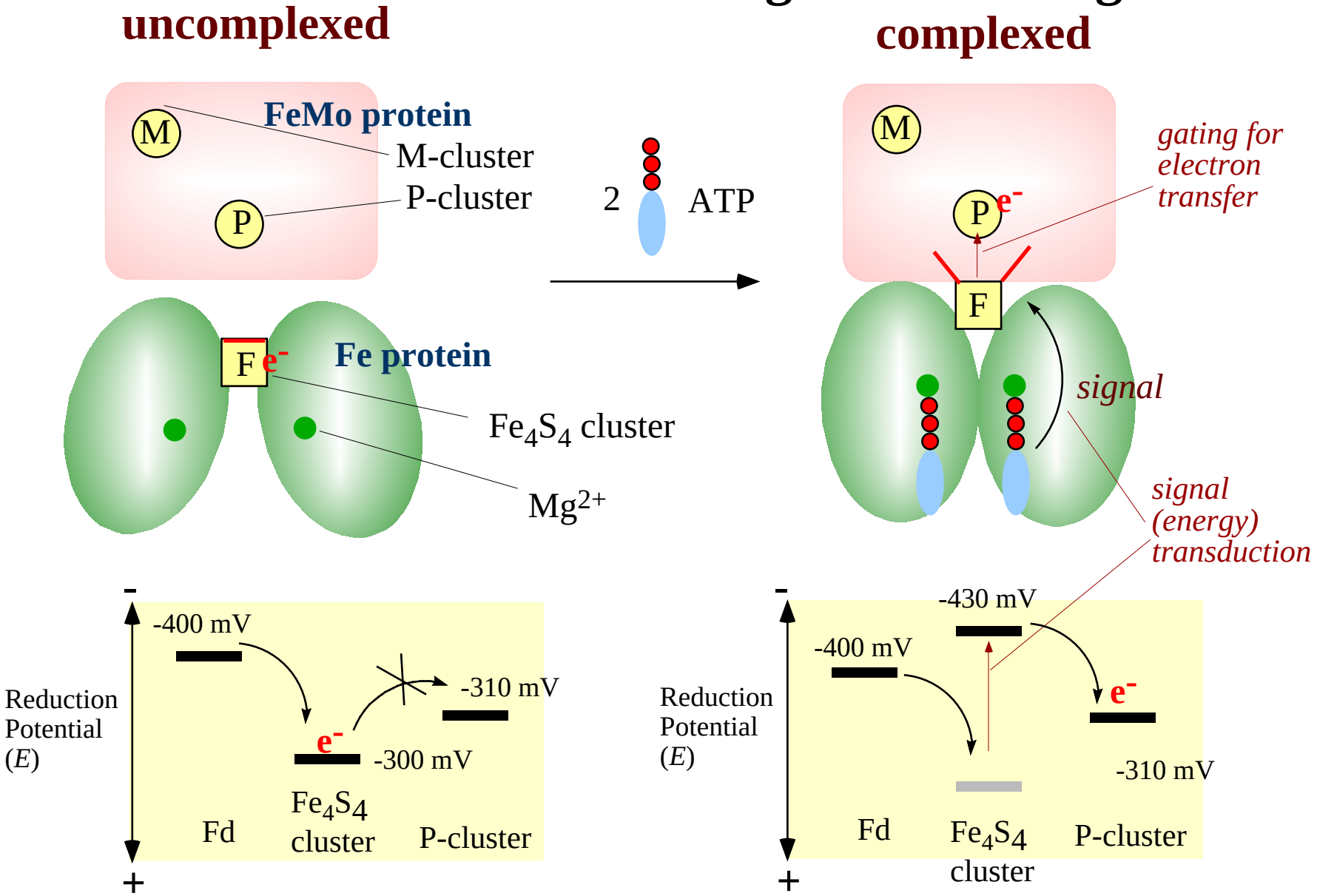
Interaction between Fe protein and FeMo protein



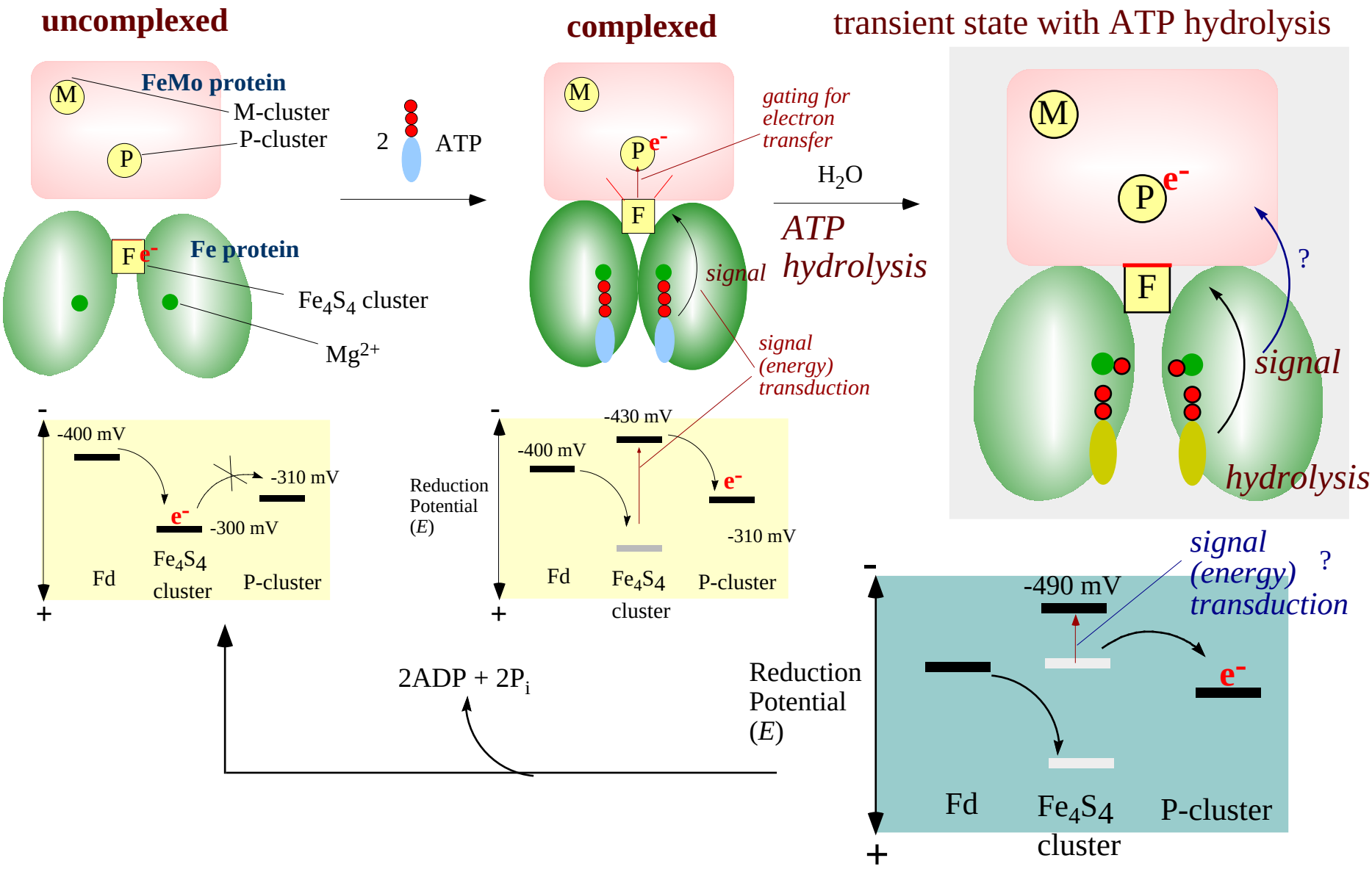
Residues parcipitating in Fe protein/FeMo protein interactions have their Ca atoms highlighted as black spheres.

Signal transduction and electron transfer pathway in the nitrogenase complex.

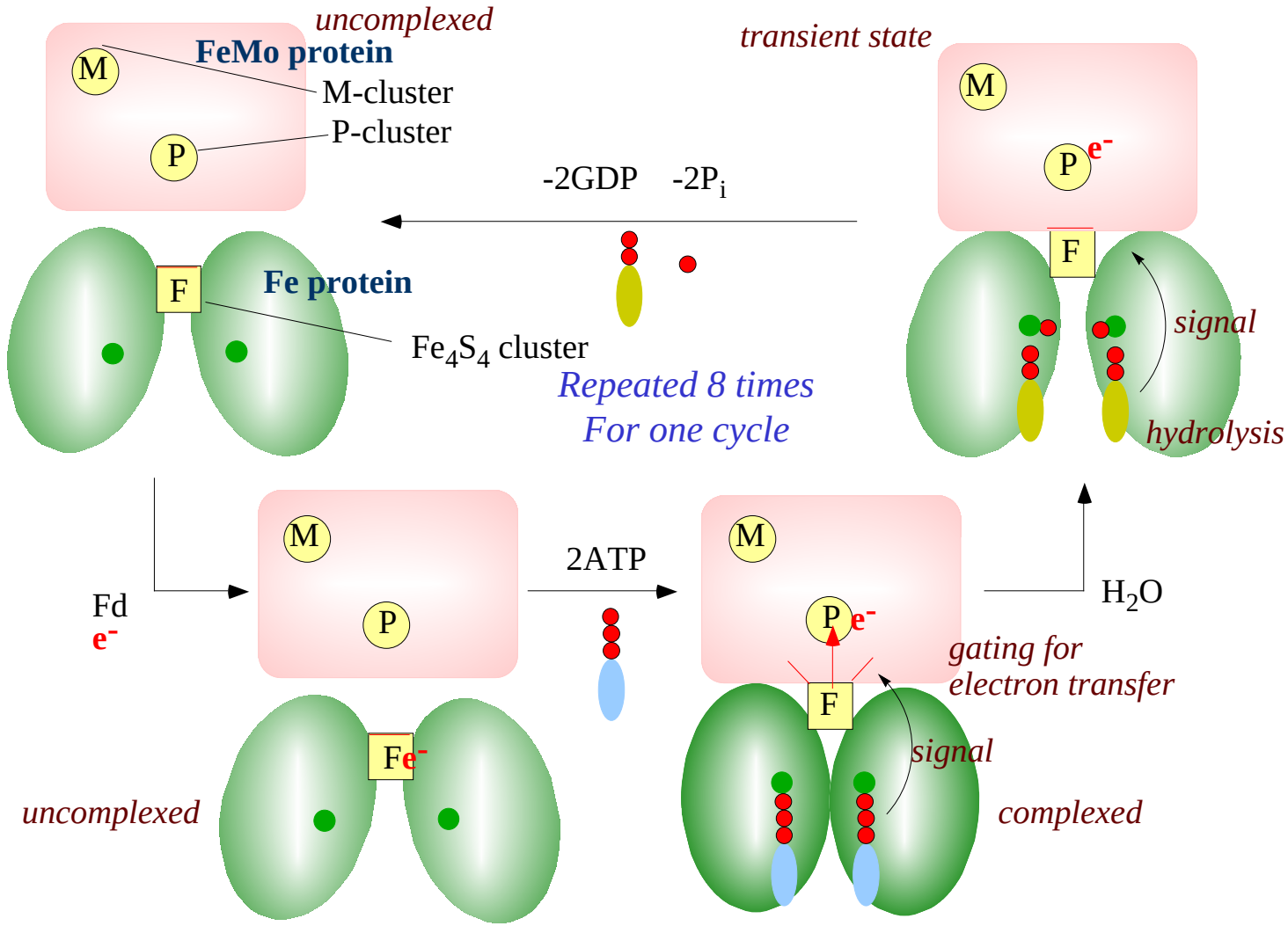
A Model for Complexation between Fe Protein and FeMo Protein with Mg·ATP Binding



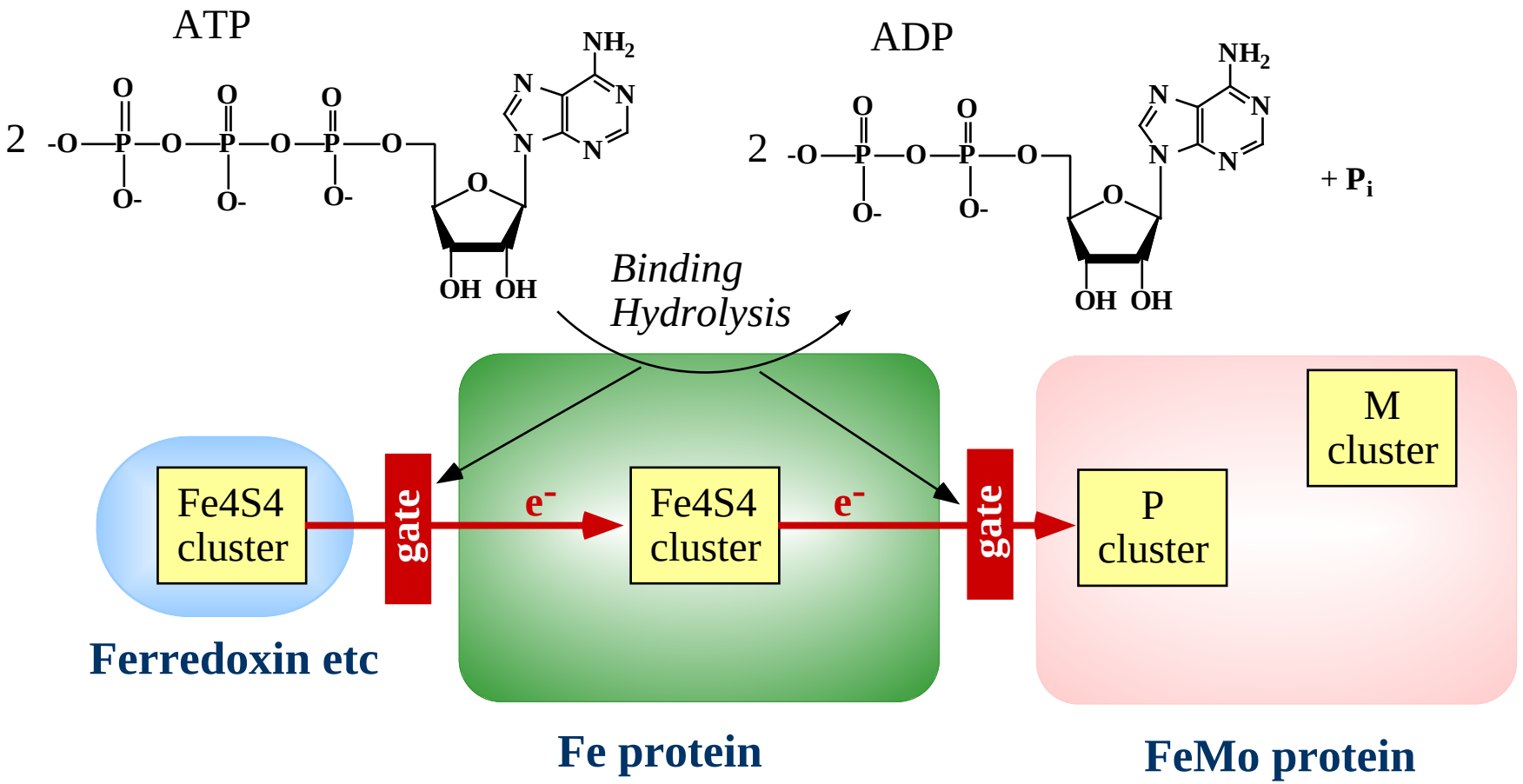
A Model for Electron Transfer from Fe Protein to FeMo Protein with ATP Hydrolysis



Plausible Mechanism for Signal Transduction and Electron Transfer between Fe Protein and FeMo Protein



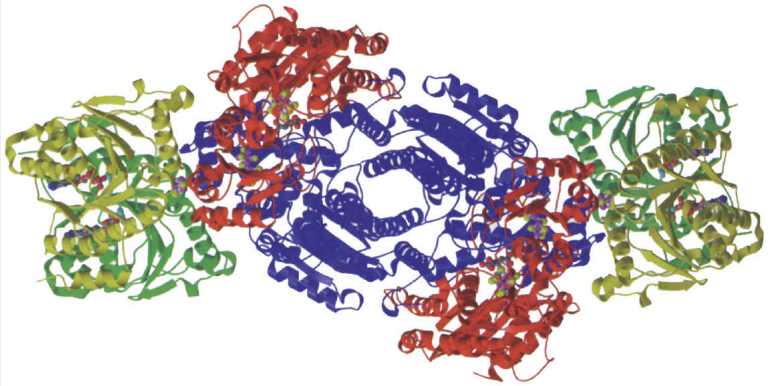
Electron Shuttle Gated by Dynamic Behavior of Fe Protein



Dynamic Behavior

Allosteric Effect, Signal Transduction

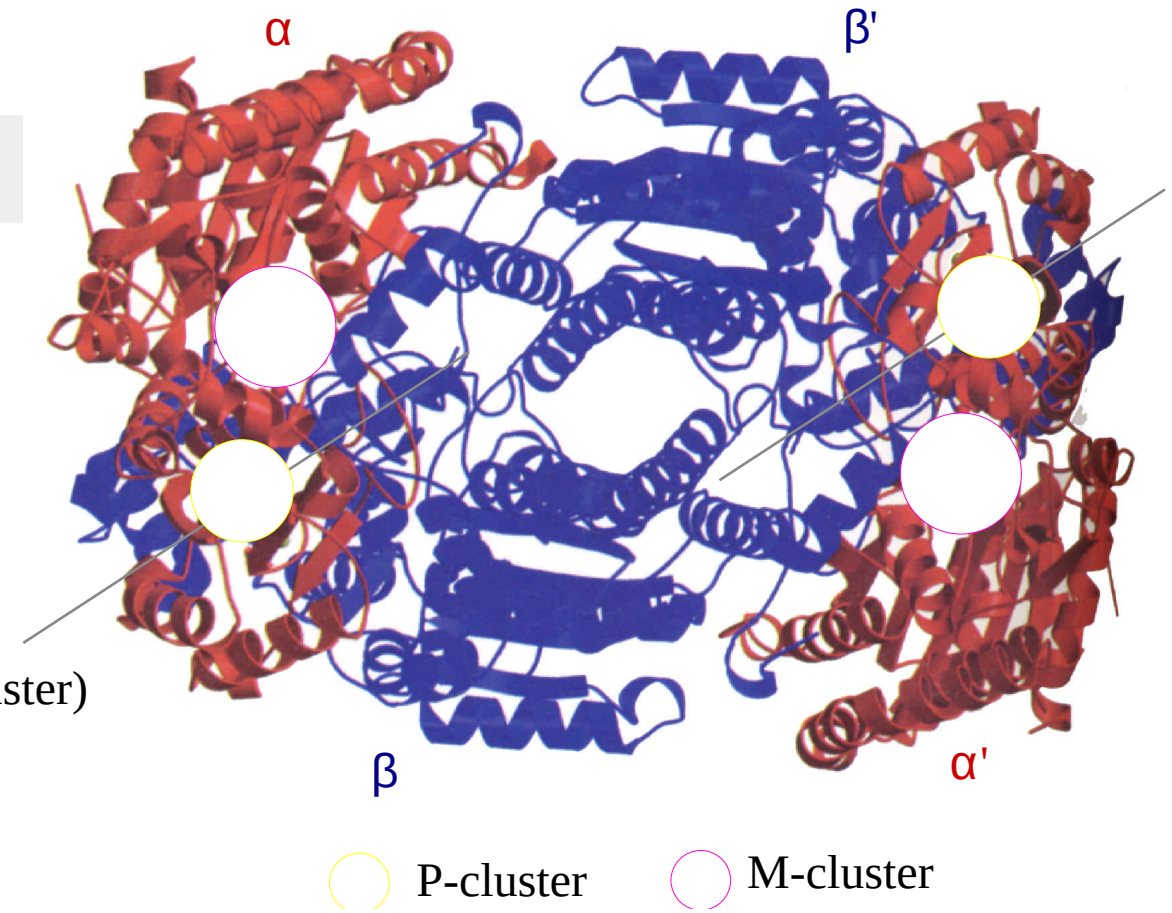
FeMo Protein of Nitrogenase Complex



Nitrogenase Complex
from *Azotobacter vinelandii*

FeMo Protein

Nature 1997
PDB 2MIN



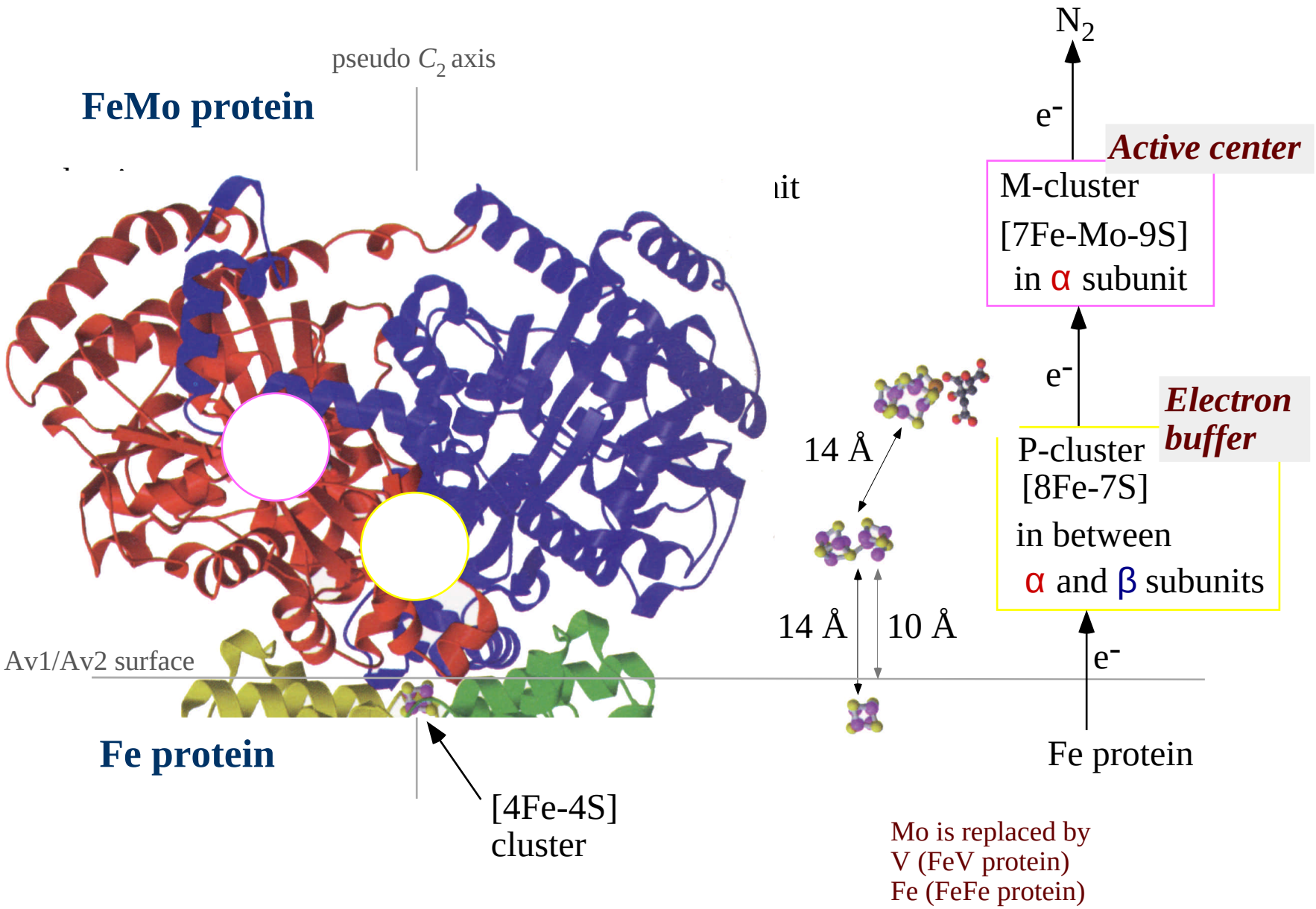
$\alpha_2\beta_2$ subunits (~240 kD)

α subunit: 491 aa

β subunit: 522 aa

Containing 30Fe and 2Mo
(two P-cluster and two M-cluster)

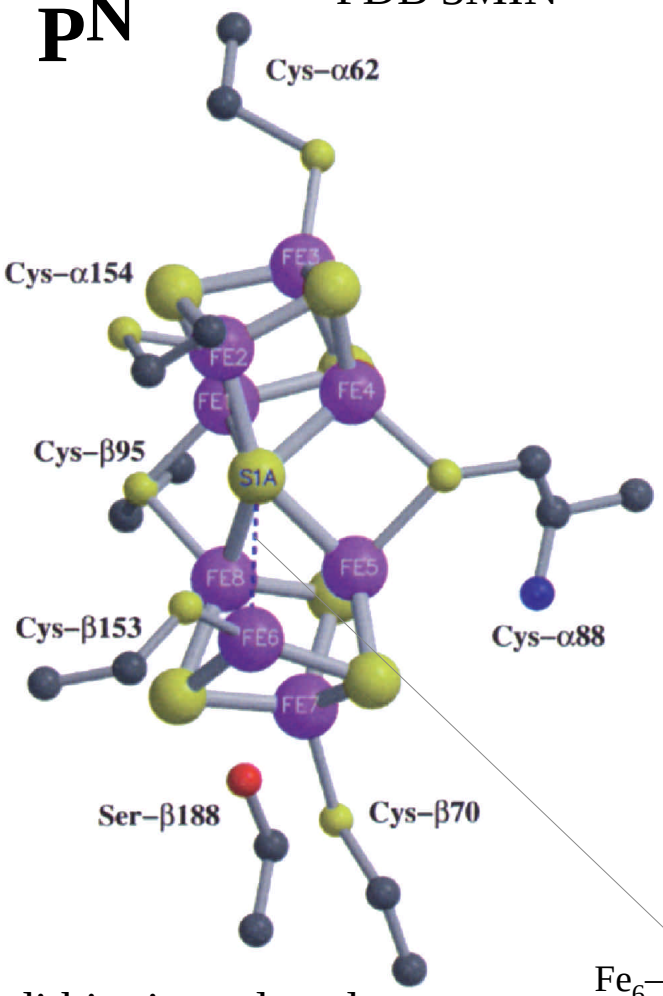
A Half of FeMo Protein from *Av* Nitrogenase Complex



Structure of P-Cluster (Reduced Form: P^N) in *A. vinelandii* MoFe Protein

P^N

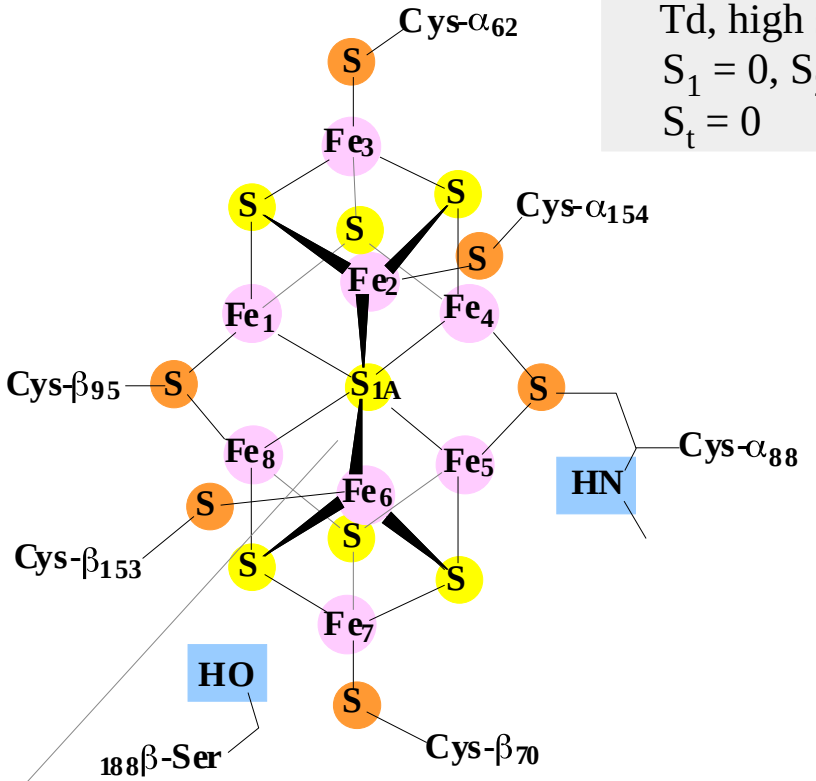
PDB 3MIN



dithionite reduced

$\{Fe_8S_7(CysS)_6\}^{4-}$

$[Fe_8S_7]^{2+}$



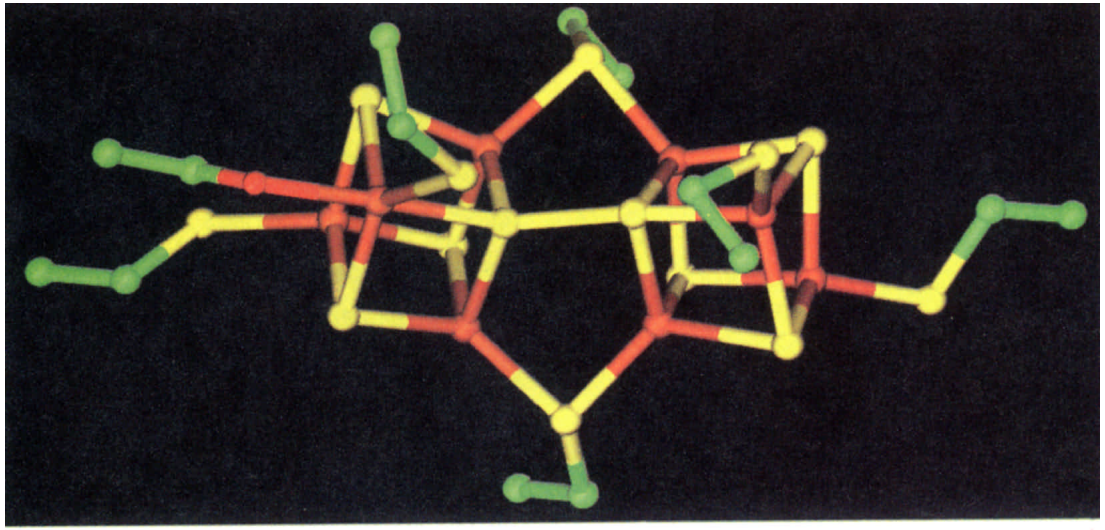
[4Fe(II), 4Fe(II)]
Td, high spin
$S_1 = 0, S_2 = 0$
$S_t = 0$

$Fe_6–S_{1A}$ = 2.92 Å (3MIN)
= 2.47 Å (1QH1: Kp1)

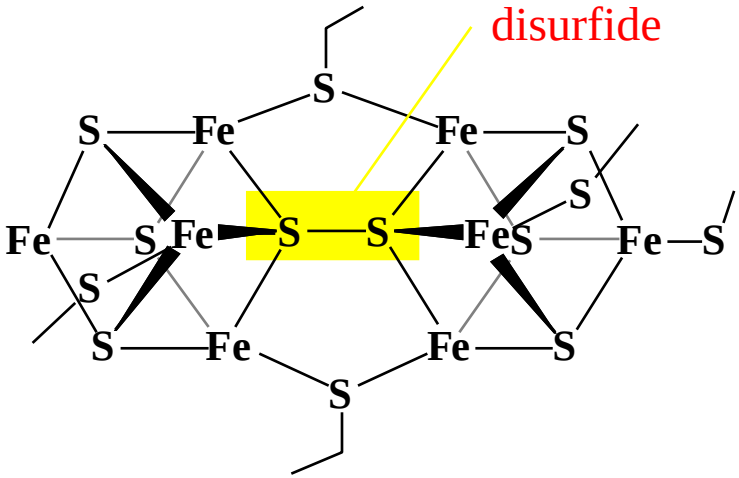
Fe···Fe (μ_3-S) = ~2.65 Å
Fe···Fe (μ_2-S) = ~3.75 Å

Wrongly Proposed Structure for Reduced P-Cluster

This is NOT correct !!



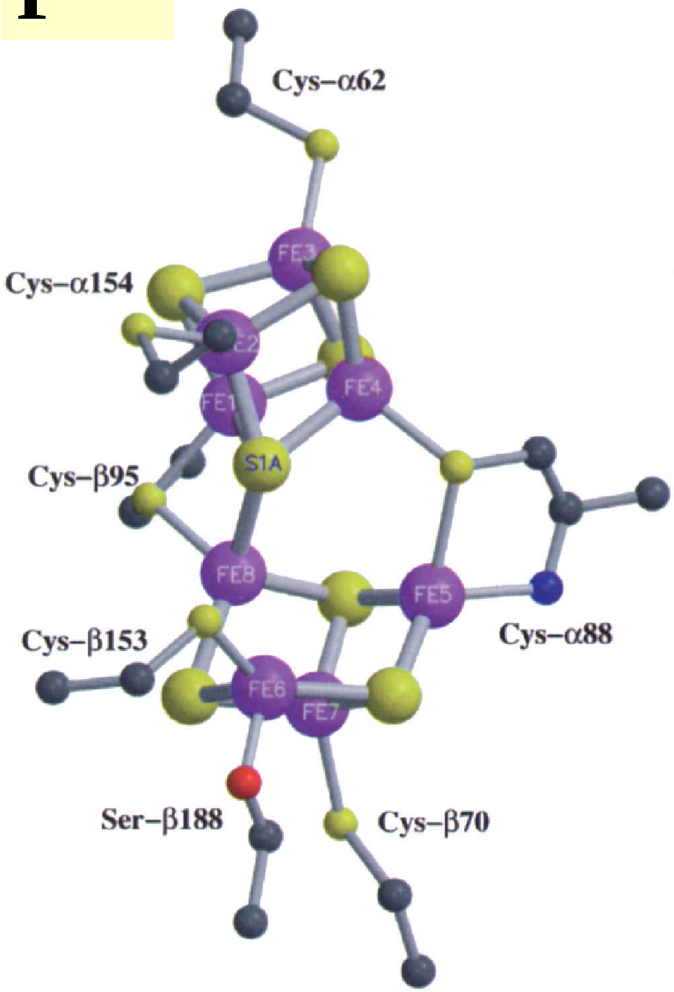
from D. Voet "Biochemistry"



Structure of P-Cluster (Oxidized Form: P^{OX}) in *A. vinelandii* MoFe Protein

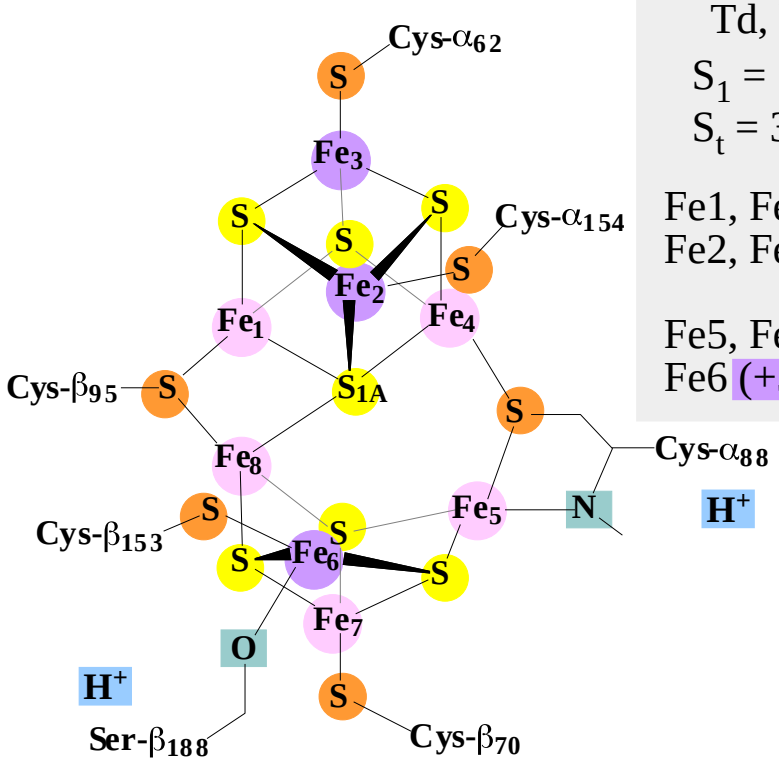
P^{OX}

PDB 2MIN



$\{Fe_8S_7(CysS)_6\}^{2-}$

$[Fe_8S_7]^{4+}$



[2Fe(II)2Fe(2.5), 3Fe(II)Fe(III)]

Td, high spin

$S_1 = 1/2$, $S_2 = 7/2$

$S_t = 3$ or 4

Fe1, Fe4 (+2.0)
Fe2, Fe3 (+2.5)

Fe5, Fe7, Fe8 (+2.0)
Fe6 (+3)

slightly longer than P^N.

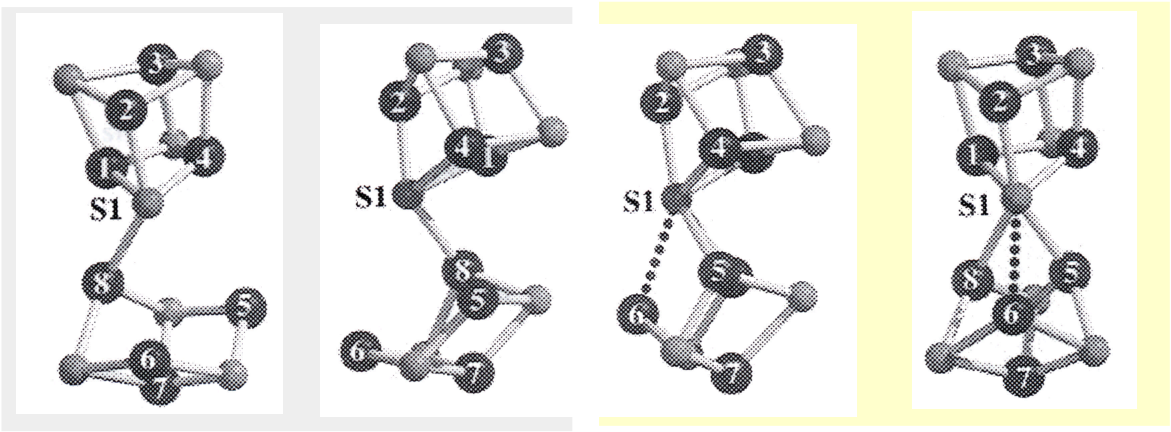
Fe···Fe (μ_3-S) = ~2.65 Å
Fe···Fe (μ_2-S) = ~3.75 Å

Fe_5 and Fe_6 moved by ~1.4 Å away from S_{1A}

Structural Parameters for P^{OX} and P^{N}

C. Rees et al. *Biochemistry* 1997, 36, 1181

P^{OX}



P^{N}

Table 3: Metal−Metal and Metal−Sulfur S1 Distances in the P^{OX} and P^{N} States of the P-Cluster (in Angstroms)[a]

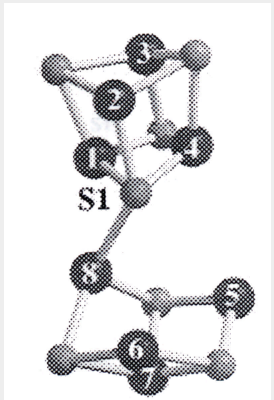
	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Fe8	S1
Fe1		2.42	2.70	2.53	3.77	4.76	5.42	3.05	2.26
Fe2	2.43 (+0.01)		2.76	2.54	4.59	5.02	6.64	4.46	2.34
Fe3	2.71 (+0.01)	2.78 (+0.02)		2.59	5.37	6.83	7.61	5.57	3.97
Fe4	2.48 (−0.05)	2.61 (+0.07)	2.69 (+0.10)		3.03	4.70	5.57	4.06	2.23
Fe5	4.80 (+1.03)	5.78 (+1.19)	6.23 (+0.86)	3.77 (+0.74)		2.56	2.66	2.46	2.43
Fe6	5.72 (+0.94)	6.07 (+1.05)	7.90 (+1.07)	5.64 (+0.94)	3.88 (+1.32)		2.65	2.52	2.92
Fe7	5.43 (+0.01)	6.76 (+0.12)	7.69 (+0.08)	5.57 (0.0)	2.76 (+0.10)	2.77 (+0.12)		2.62	4.31
Fe8	2.96 (+0.09)	4.37 (+0.11)	5.51 (−0.06)	3.89 (+0.17)	3.41 (+0.95)	3.22 (+0.70)	2.72 (+0.10)		2.45
S1	2.27 (+0.01)	2.30 (−0.04)	4.06 (+0.09)	2.26 (+0.03)	3.81 (+1.38)	3.86 (+0.94)	4.42 (+0.11)	2.32 (−0.13)	

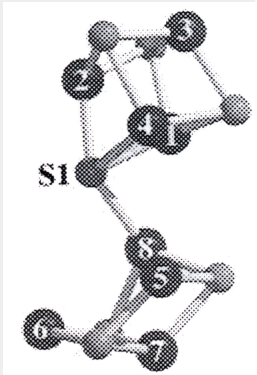
[a] Distances between pairs of metal atoms are indicated for the P^{N} state (upper right) and P^{OX} state (lower left). The distances are the average of the two P-clusters in the crystallographic asymmetric unit of the *A. vinelandii* MoFe-protein. The average deviation between crystallographically independent metal−metal distances is 0.05 Å, with a maximum of 0.11 Å for the Fe1−Fe6 pair in P^{N}. The numbers in parantheses in the lower left indicate the change in average distance upon oxidation of P^{N} to P^{OX}.

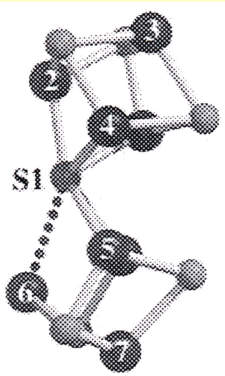
Structural Parameters for P^{OX} and P^{N}

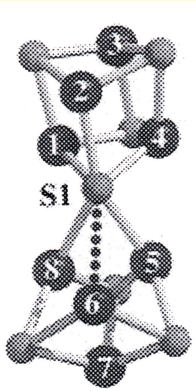
C. Rees et al. *Biochemistry* 1997, 36, 1181

P^{OX}







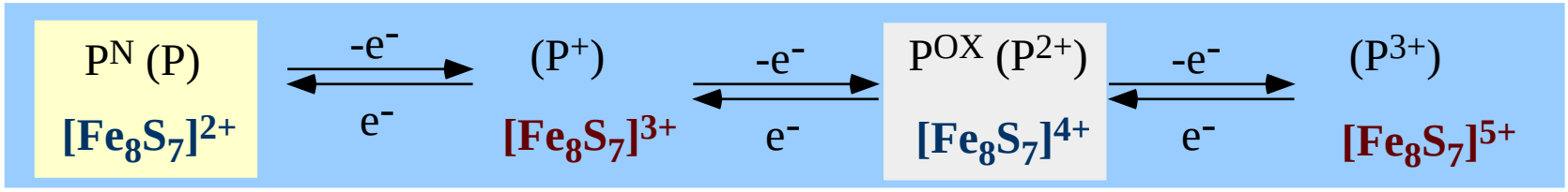


P^{N}

Bond Lengths for P^{N} and P^{OX} in Å

Bond	P^{OX}	P^{N}	$\Delta(P^{OX} - P^{N})$
Fe1–Fe2	2.43	2.42	+0.01
Fe2–Fe3	2.78	2.76	+0.02
Fe3–Fe4	2.69	2.59	+0.10
Fe4–Fe5	3.77	3.03	+0.74
Fe5–Fe6	3.88	2.56	+1.32
Fe6–Fe7	2.77	2.65	+0.12
Fe7–Fe8	2.72	2.62	+0.10
Fe5–S1	3.81	2.43	+1.38
Fe6–S1	3.86	2.92(2.47)	+0.94

Redox Behavior of P-Cluster in *Av* MoFe Protein



$S_t = 0$

$[Fe^{II}_2Fe^{III}_2]$ (S = 0)

$[Fe^{II}_2Fe^{III}_2]$ (S = 0)

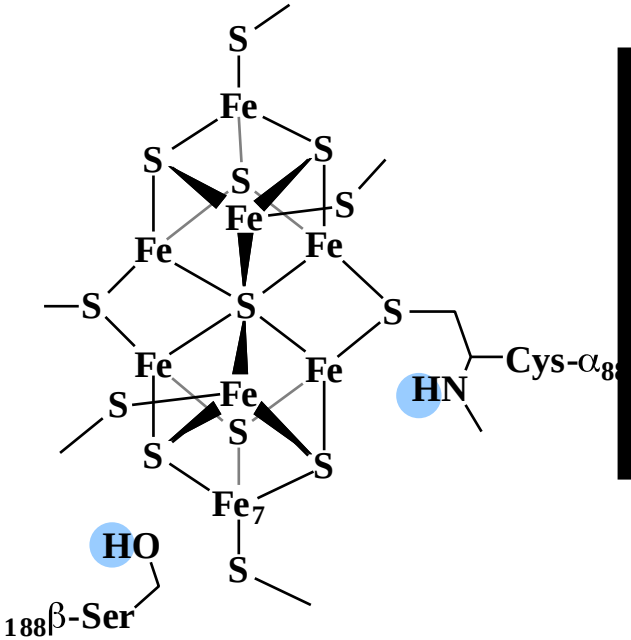
$S_t = 1/2$ or $5/2$

$S_t = 3$ or 4

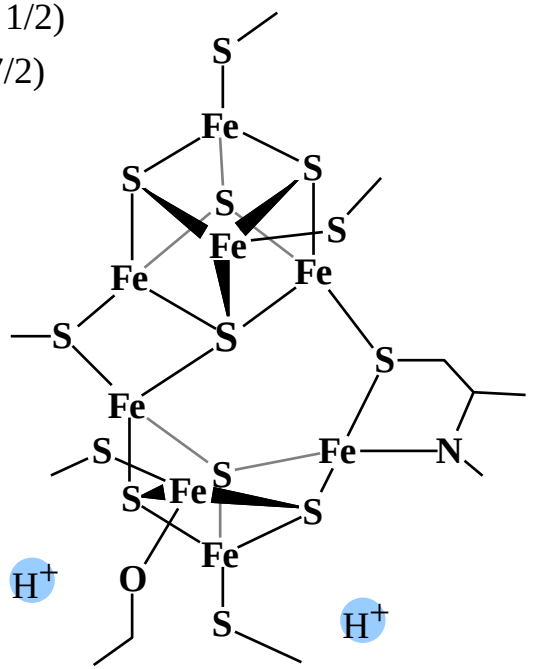
$[Fe^{II}_2Fe^{2.5}_2]$ (S = 1/2)

$[Fe^{II}_3Fe^{III}]$ (S = 7/2)

$S_t = 1/2$ or $7/2$

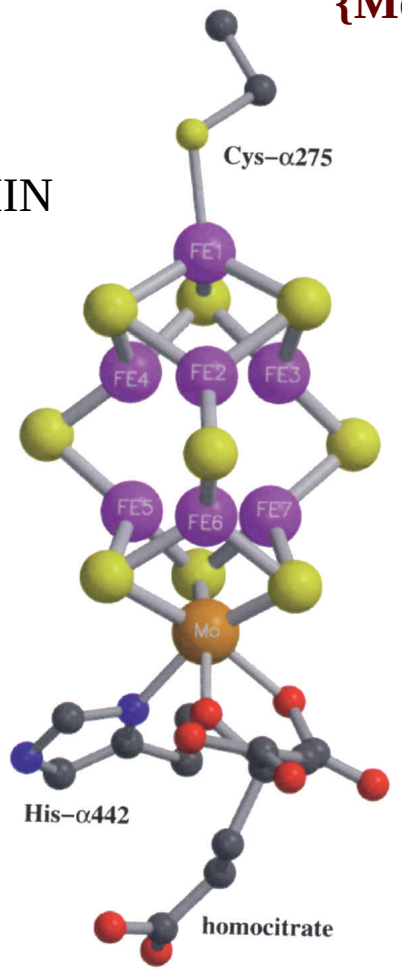


- Electron Buffer
- Electron transfer coupled with Proton transfer
- Signal transduction from Fe-protein

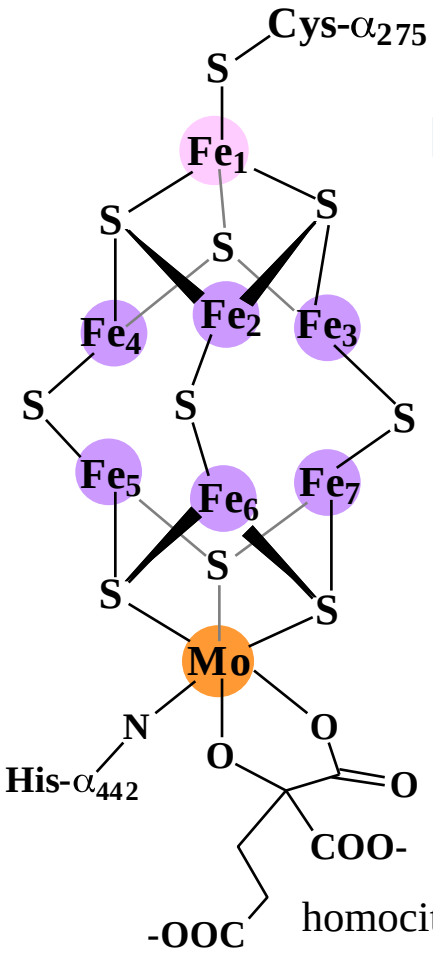


Structure of M-Cluster (FeMo Cofactor) in *A. vinelandii* MoFe Protein

PDB 2MIN



$\{MoFe_7S_9(CysS)(HisN)(hc)\}^{4-}$



Nature 1997
Biochemistry 1997

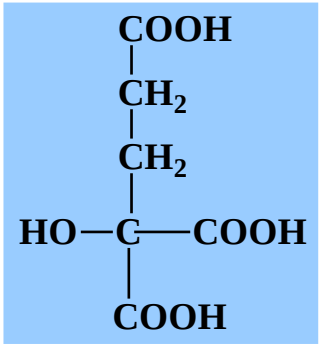
$[MoFe_8S_9]^+$ $S_t = 3/2$

$[Mo^{IV}Fe^{II}_6Fe^{III}S_9]^+$

[4Fe-3S]

[3S]

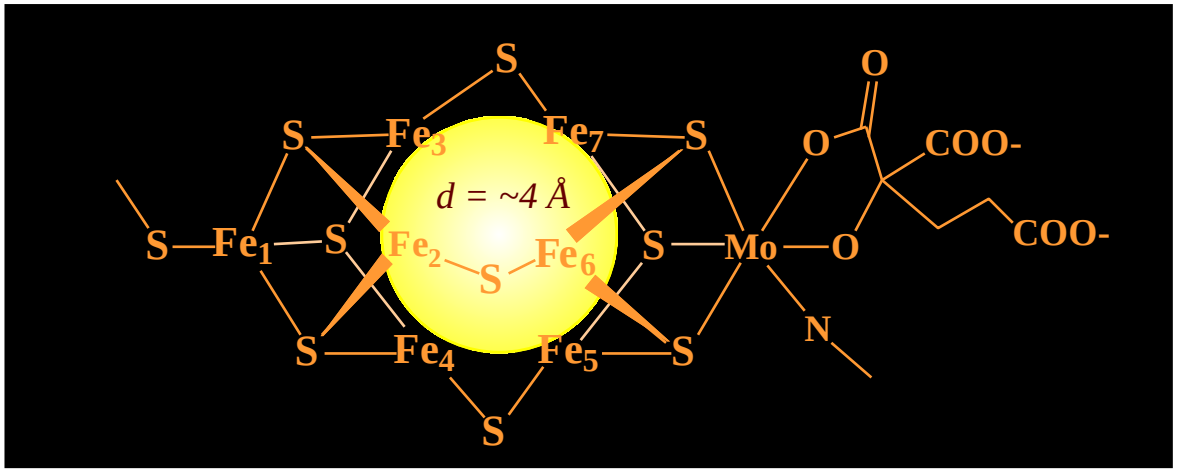
[3FeMo-3S]



buried ~10 Å from the protein surface
~14 Å away from P-cluster edge

Fe···Fe(bridge) = 2.7-2.8 Å
Fe···Fe(nonbridged) = ~3.8 Å

Structural Parameters for M^{OX} and M^{N}



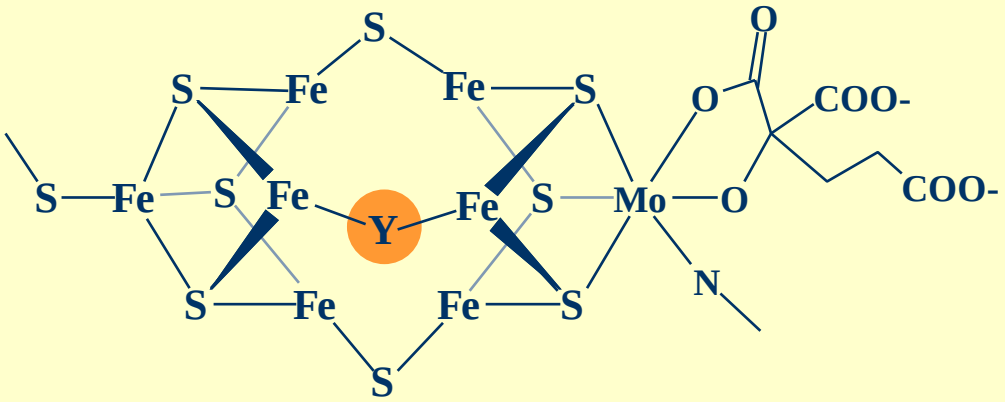
Bond Lengths for M^{N} and M^{OX} in Å

Bond	M^{OX}	M^{N}	$\Delta(M^{OX} - M^{N})$
Fe1–Fe2	2.69	2.62	+0.07
Fe2–Fe3	2.68	2.58	+0.10
Fe3–Fe4	2.65	2.56	+0.09
Fe4–Fe5	2.55	2.55	+0.00
Fe5–Fe6	2.60	2.57	+0.03
Fe6–Fe7	2.47	2.46	+0.01
Fe7–Mo	2.54	2.63	-0.09

$$P^{OX} \doteqdot P^{N}$$

C. Rees et al. *Biochemistry* 1997, 36, 1181

This is NOT Correct and Revised as Y = S

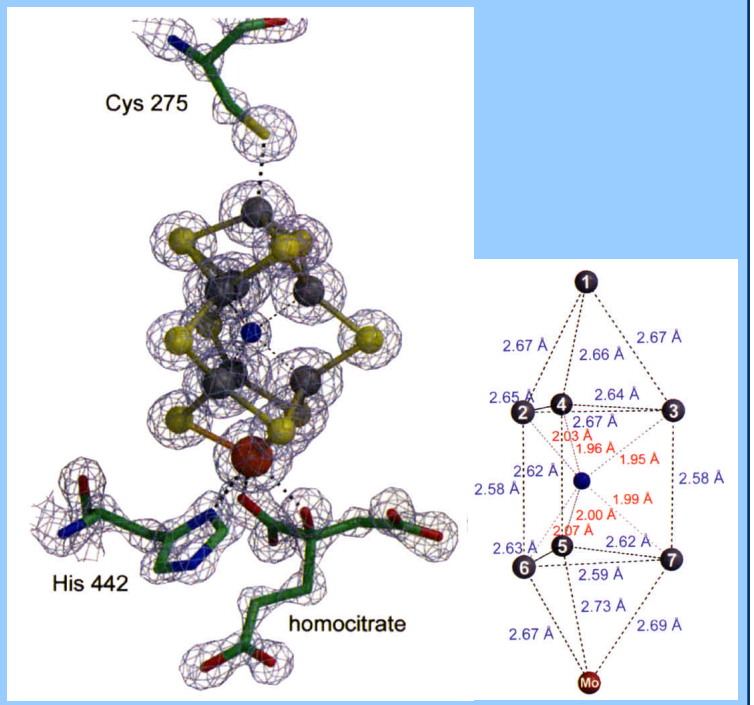


Y = O, N (not S)

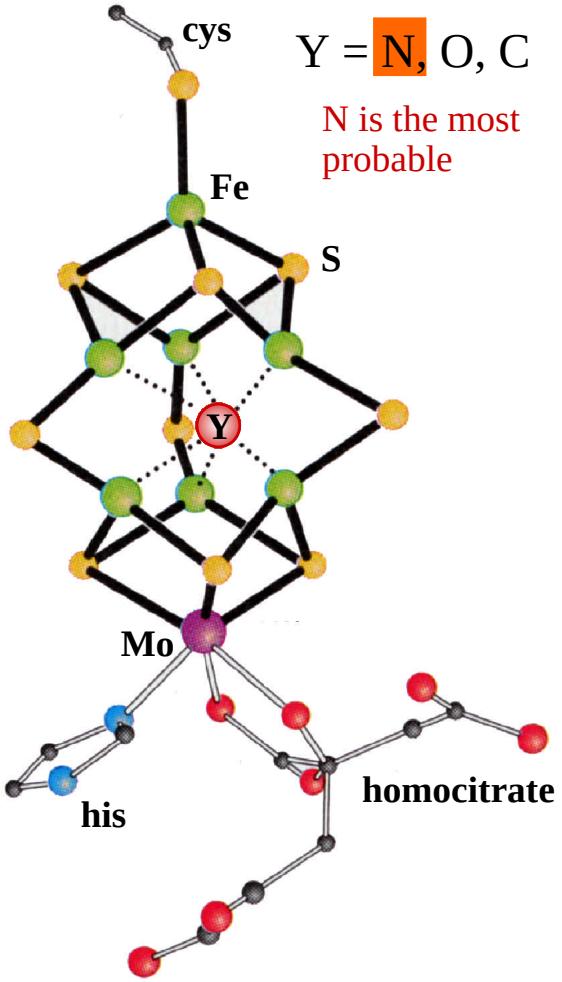
Reported in *Science* 1992, 1993 (1MIN)

And Now the Structure has been Revised as

In 2002

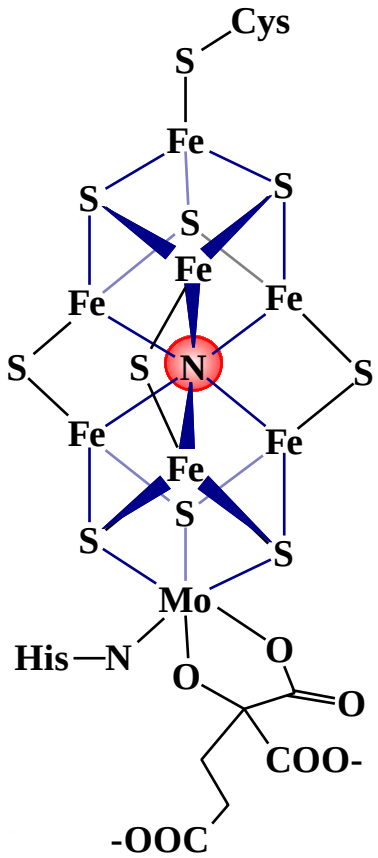


X-ray crystallography at 1.16 Å high resolution showed a central ligand in FeMo cofactor.



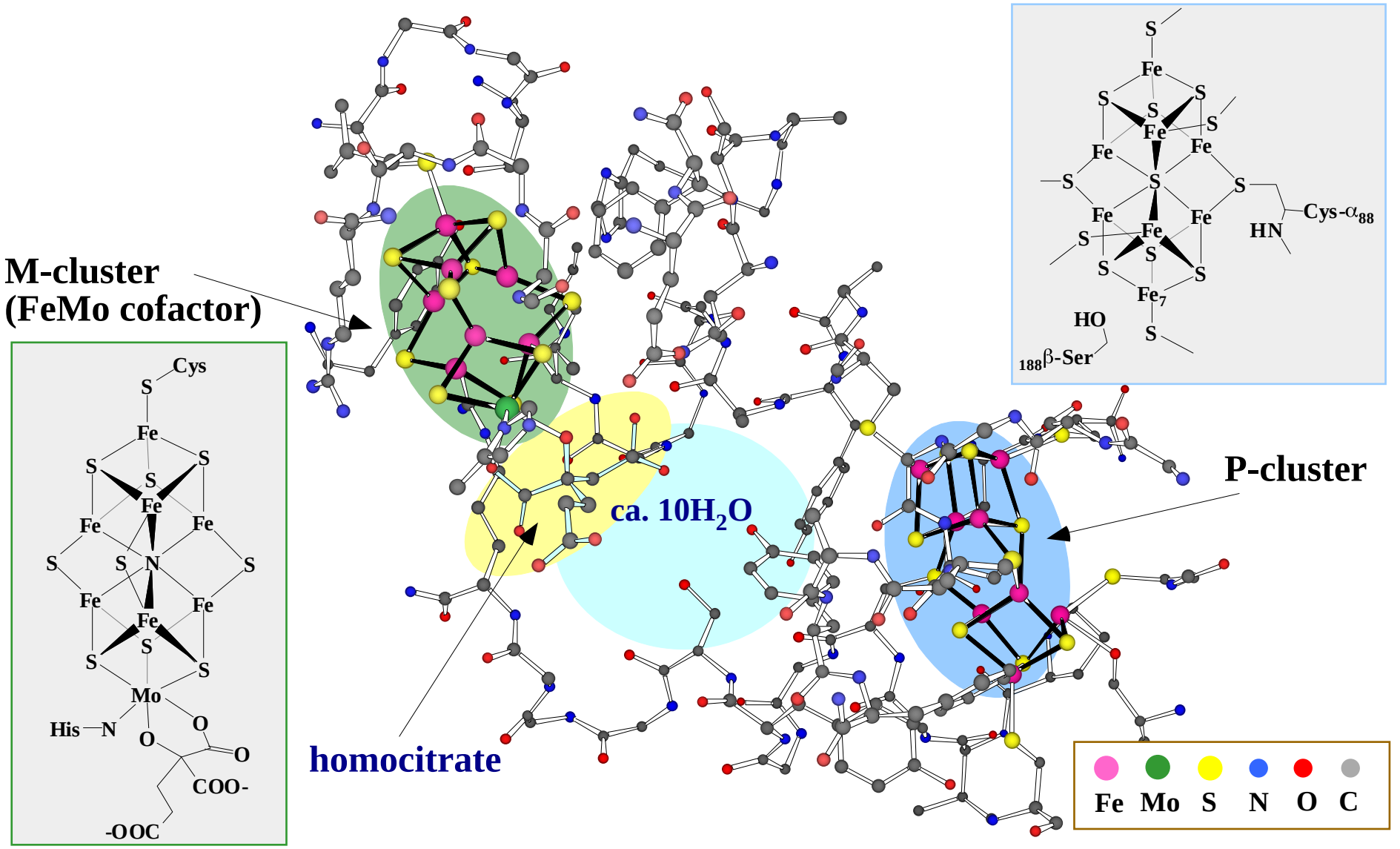
Y = N, O, C

N is the most probable

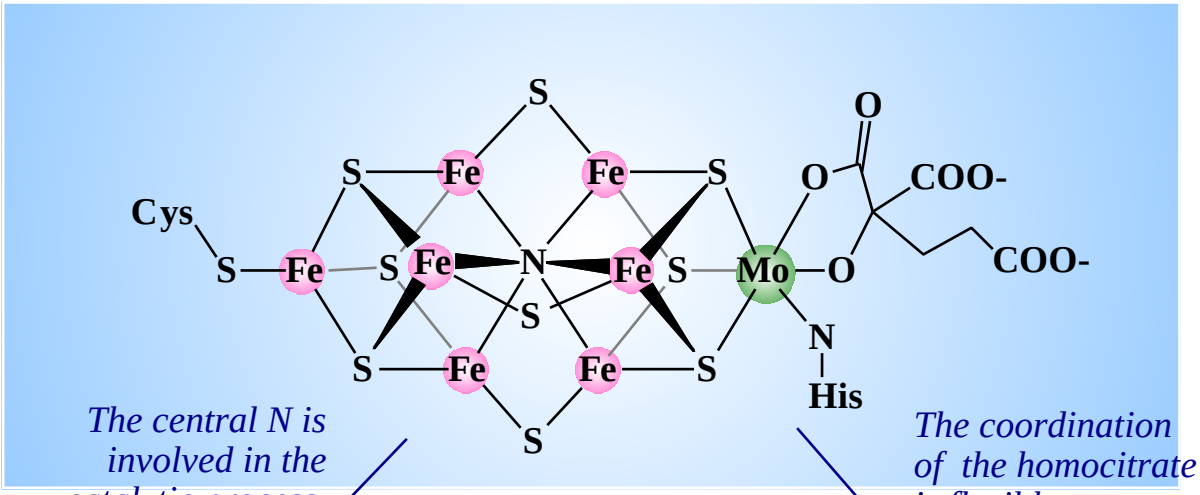


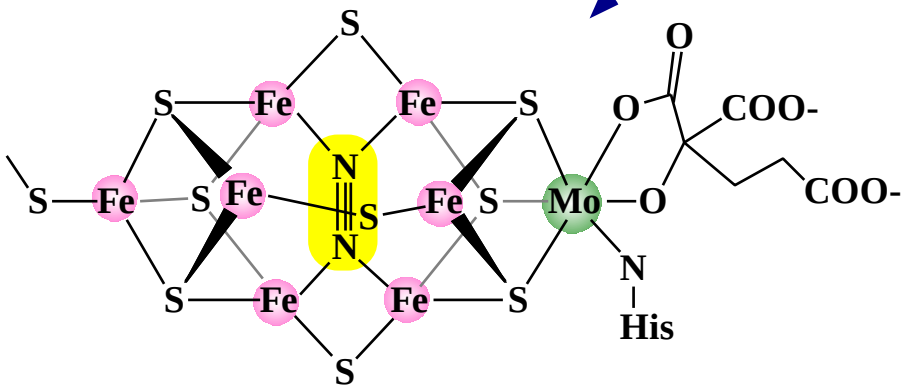
Reported by D. C. Rees et al in *Science* 2002, *297*, 1696

Arrangement of P- and M-Clusters in *Av* FeMo Protein

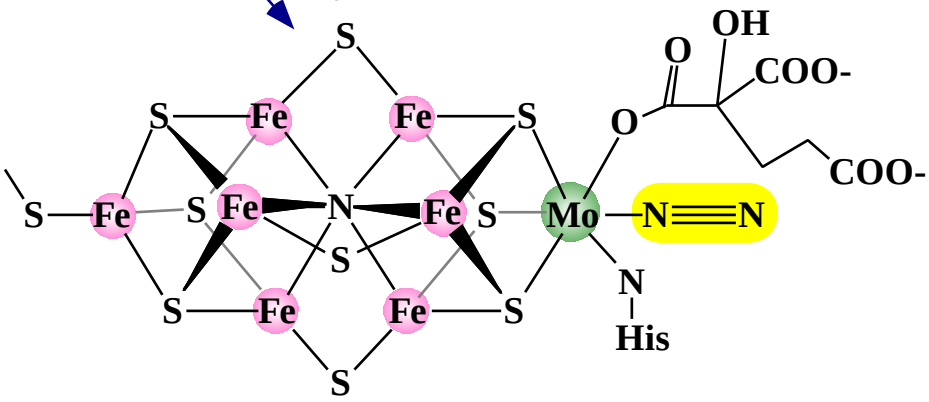


Where is the Nitrogenase Active Site ? (Dinitrogen Binding Site)





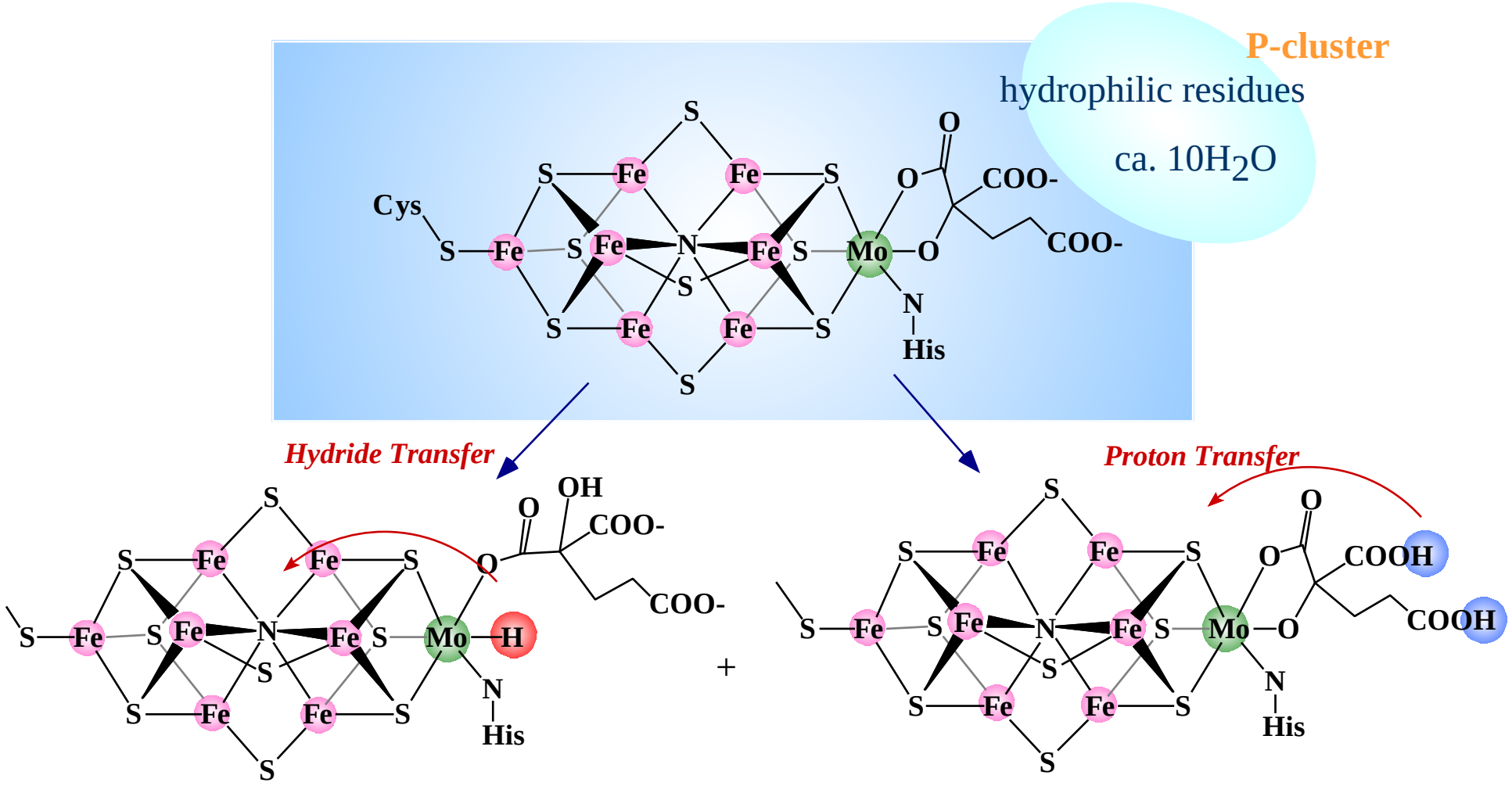
The size of the central hole is rather small for N_2, C_2H_2, N_2O, and HCN reductions.



The Mo is coordinatively saturated.
The Mo can be replaced by V and Fe.

The active site surrounded by six Fe atoms is fascinating and reasonable for multiple electron transfer and for substrate binding (TT).

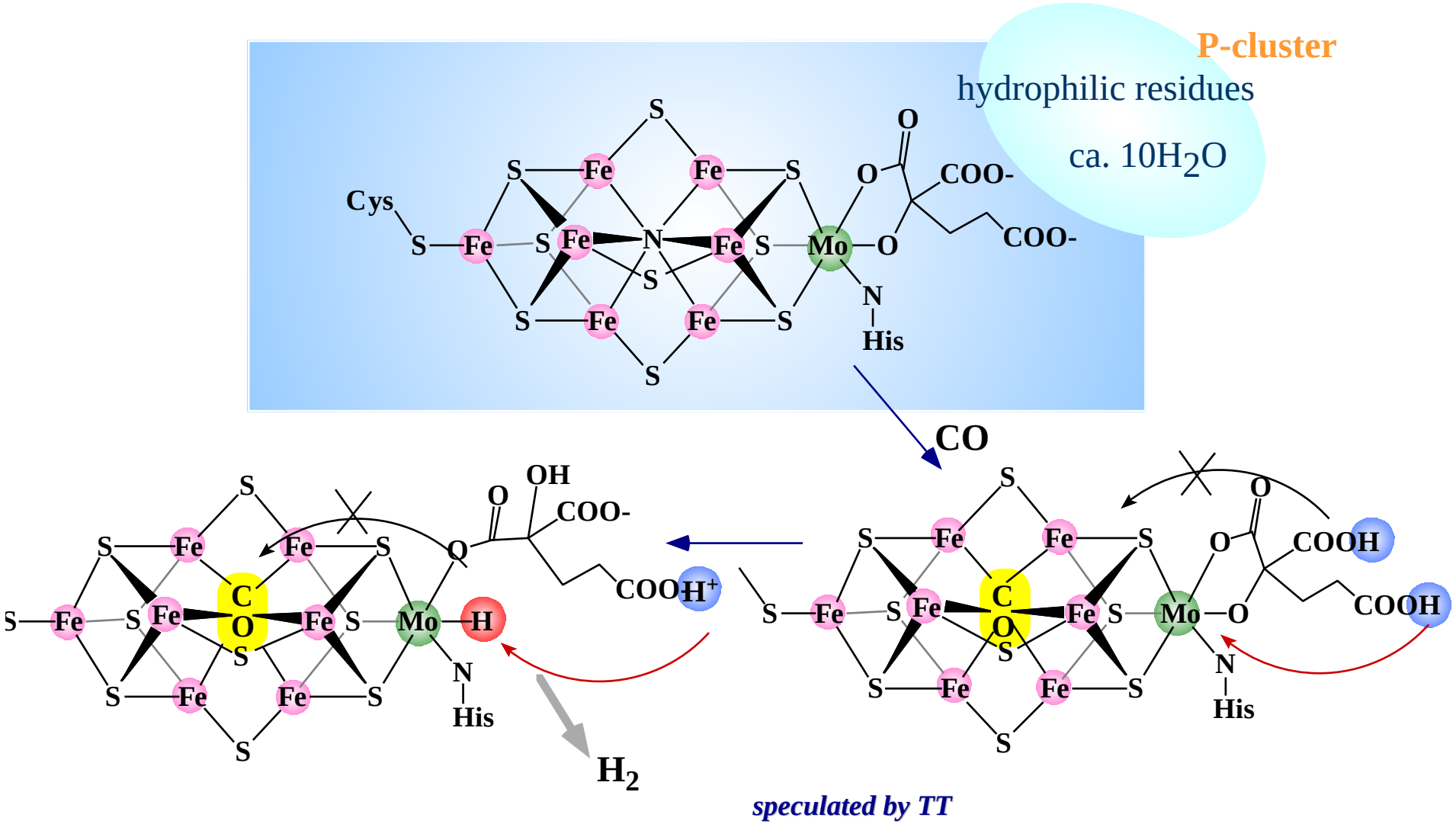
What is the Role of Homocitrate in FeMo Cofactor Site ?



speculated by TT

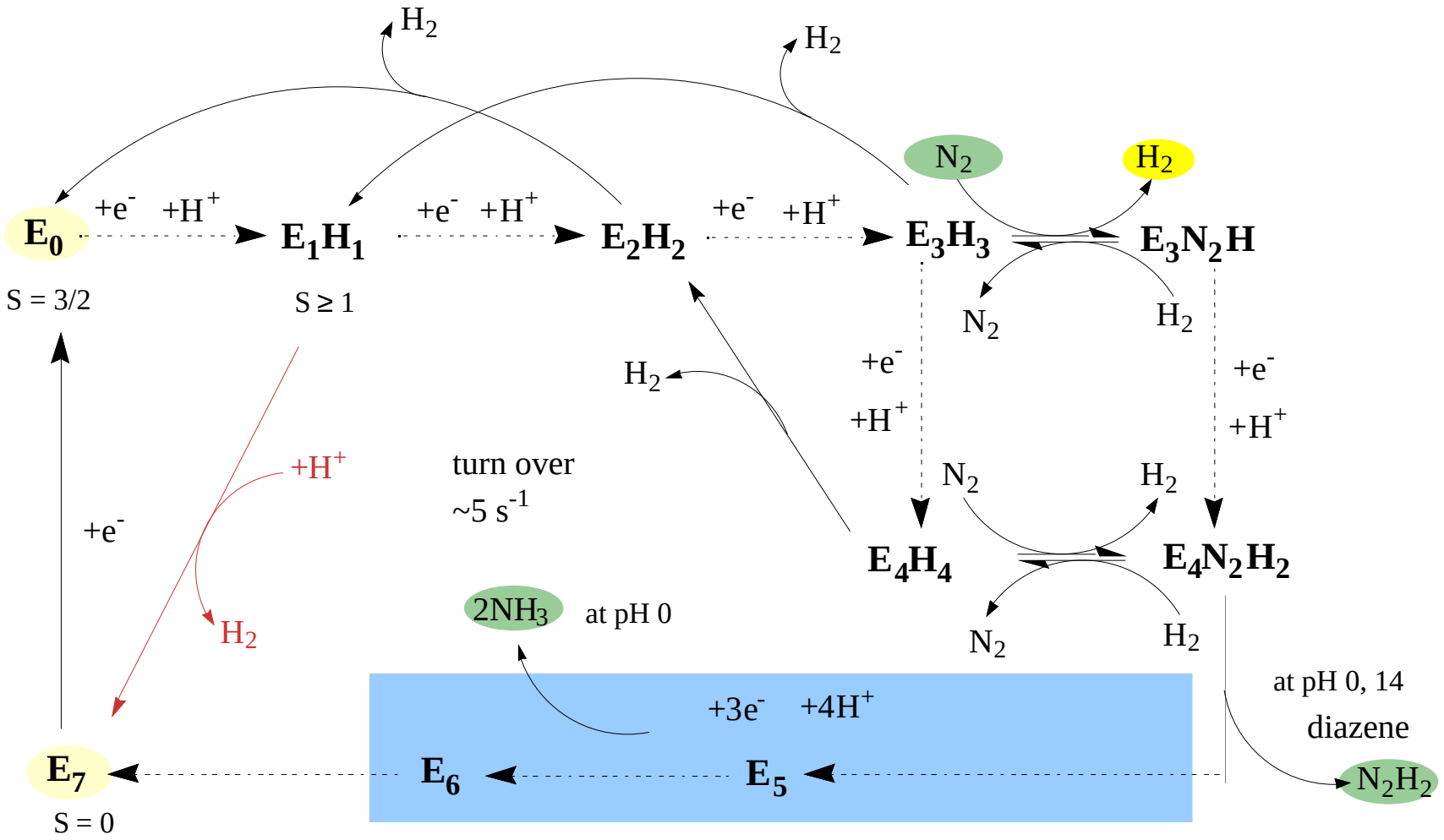
Where is the Hydrogenase Active Site ?

CO inhibited the nitrogenase activity (NH_3 generation) but allowed the hydrogenase activity (H_2 generation).



speculated by TT

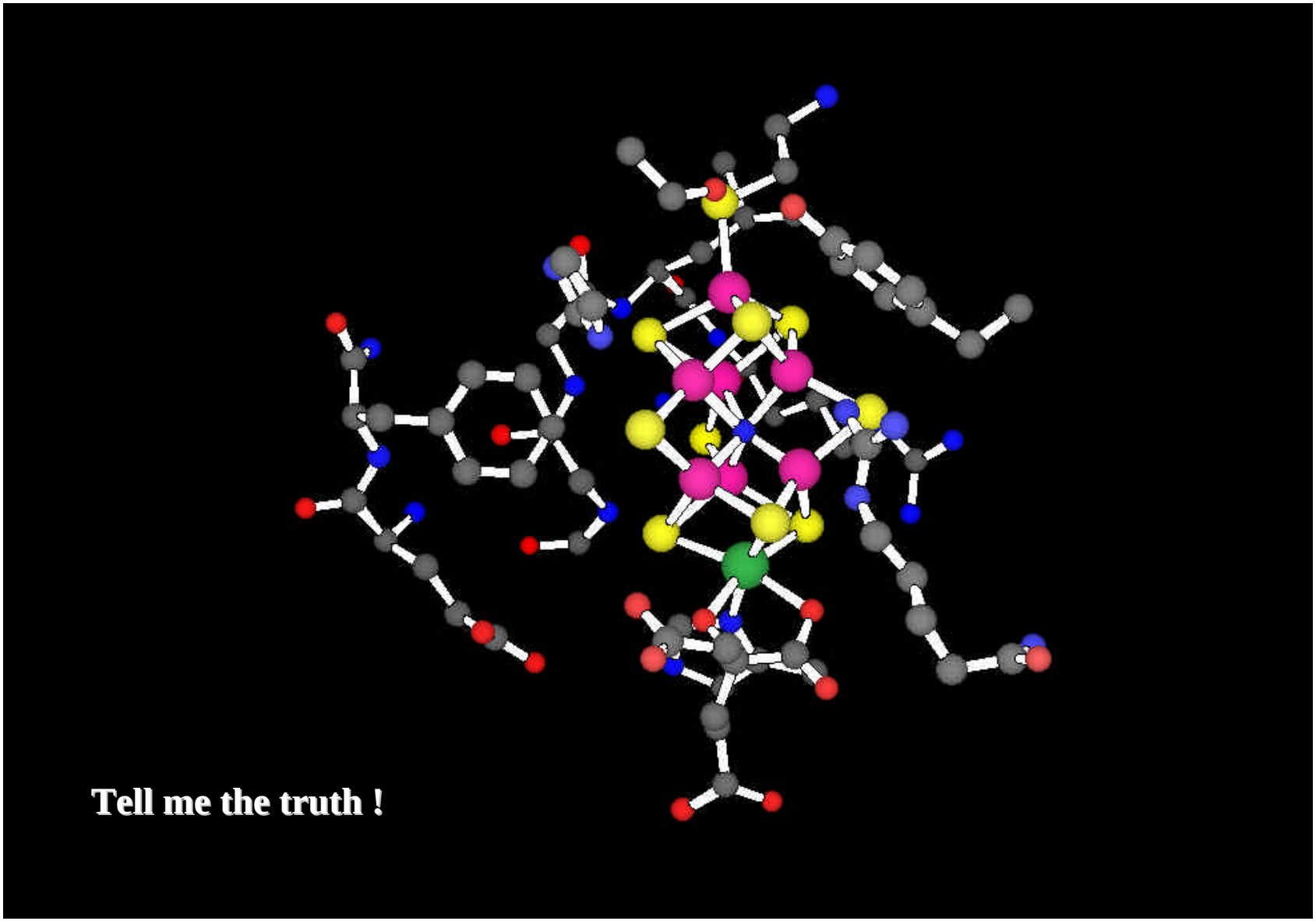
Proposed Catalytic Cycle of Nitrogenase



Proposed by kinetic studies for *Klebsiella pneumoniae* nitrogenase.

Thorneley and Lowe, *J. Biol. Inorg. Chem.*, 1996, 1, 576.

FeMoCofactor of Av Nitrogenase



Synthetic Model Compounds for Nitrogenase

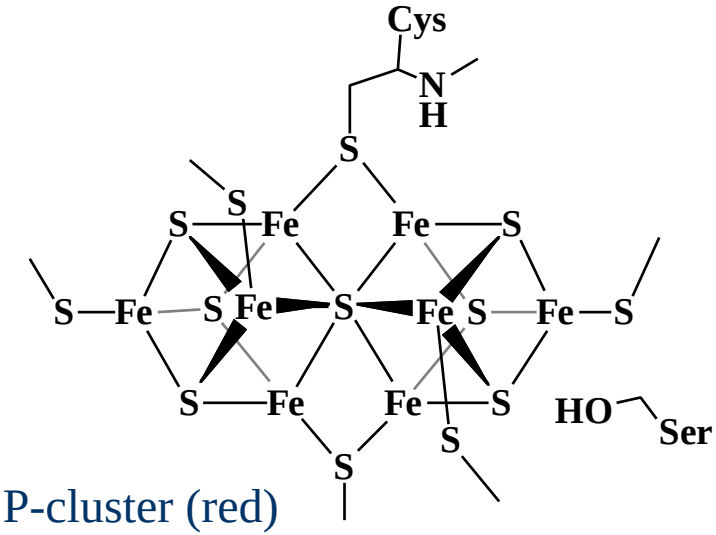
Structural Model

Design of a molecule that mimics the assumed structure of the enzyme active site. Such a model is considered totally successful if it carries out the desired function.

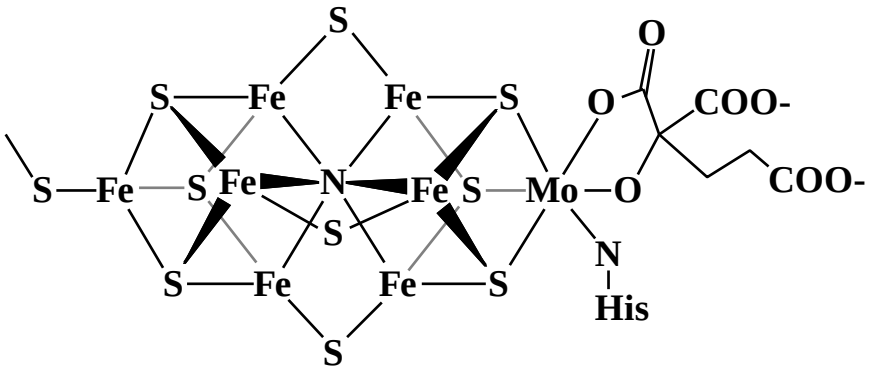
Functional Model

Synthesis of a chemically similar or dissimilar molecule that will mimic the desired function of the enzyme.

Structural Models for P-Cluster and FeMo Cofactor of Nitrogenase



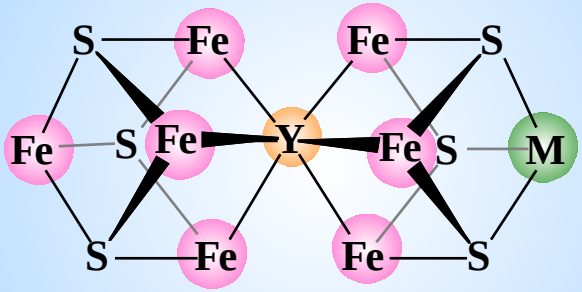
P-cluster (red)



M-cluster

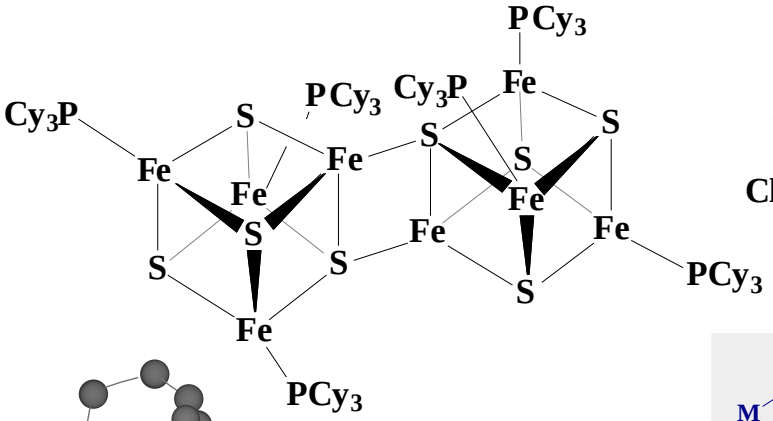
Targeted Motif

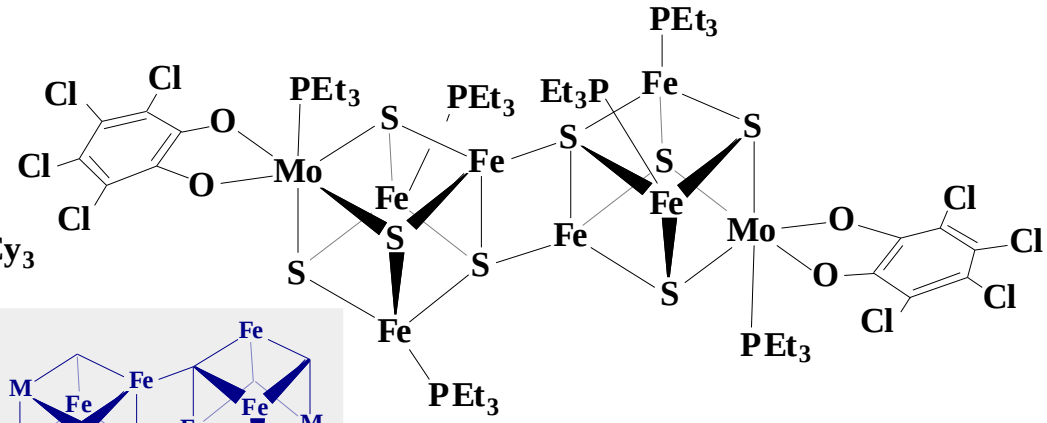
Double Cubane

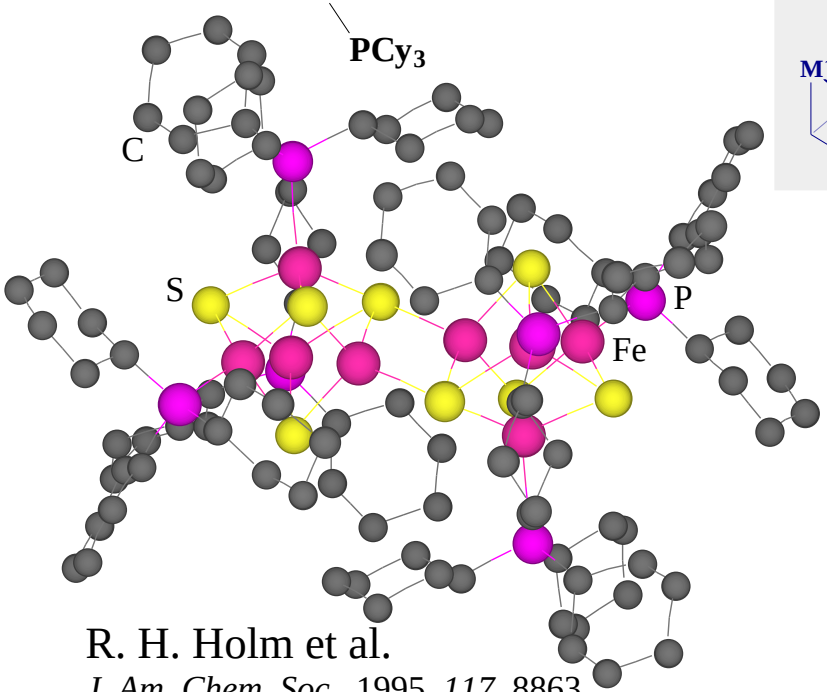


M = Fe, Mo, V
Y = S, N, O

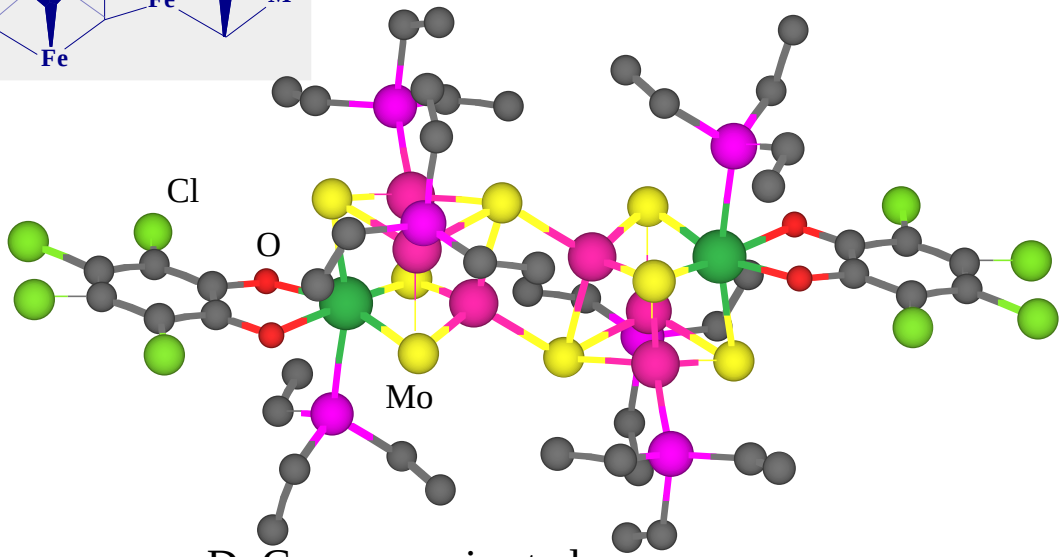
Double Cuboidal Iron-Sulfur Clusters





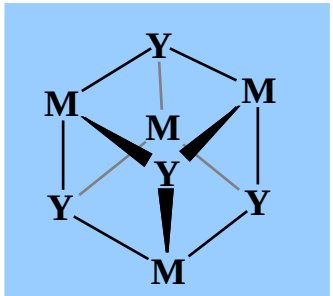


R. H. Holm et al.
J. Am. Chem. Soc., 1995, *117*, 8863
J. Am. Chem. Soc., 1996, *118*, 11844



D. Coucouvanis et al.
J. Am. Chem. Soc., 1995, *117*, 7832

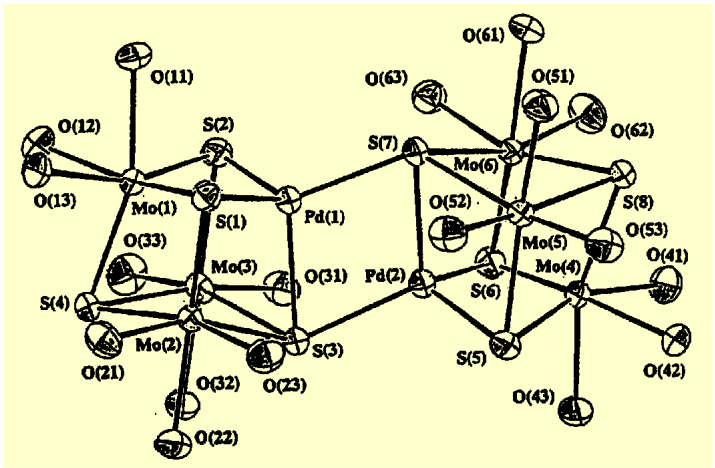
Construction of Double Cubanes from Single Cuboidal Compounds



Single Cubane

M = Fe, Mo, W
Y = S, O

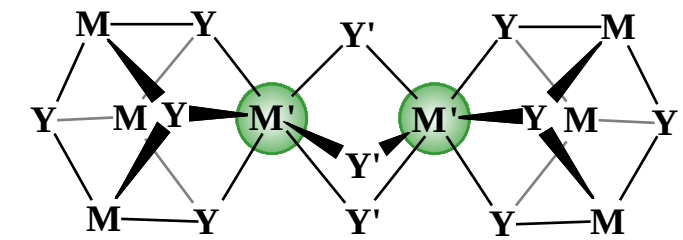
ex $[Fe_4S_4Cl_4]^{2-}$

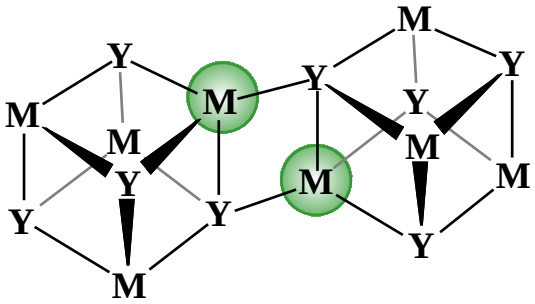


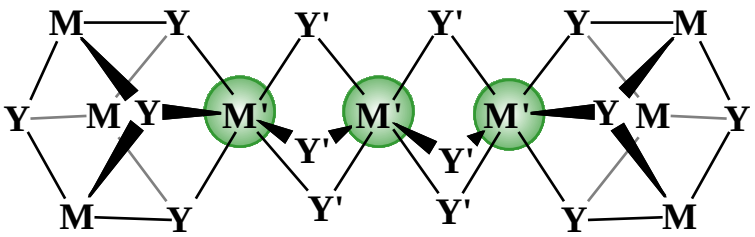
TT contributed

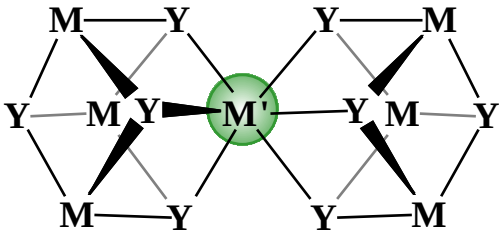
$[Pd_2Mo_6S_8]$

M. Hidai et al.
J. Am. Chem. Soc.
1992









M' = Fe, Mo, W, V; Y = S, O

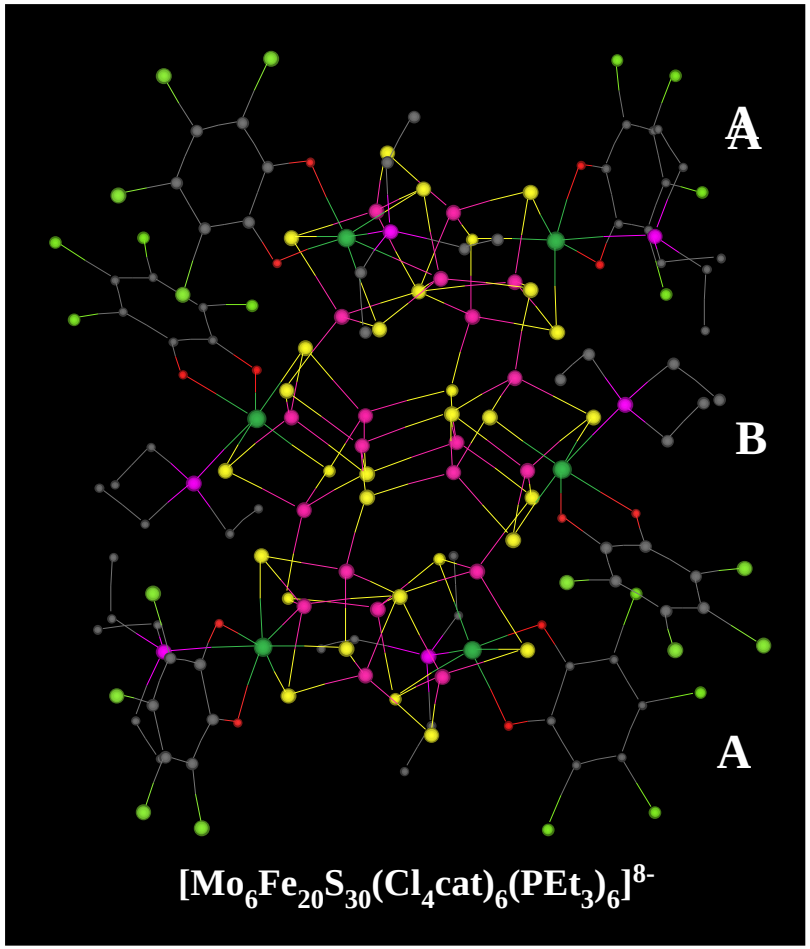
A Structural Model for P-Cluster of Nitrogenase

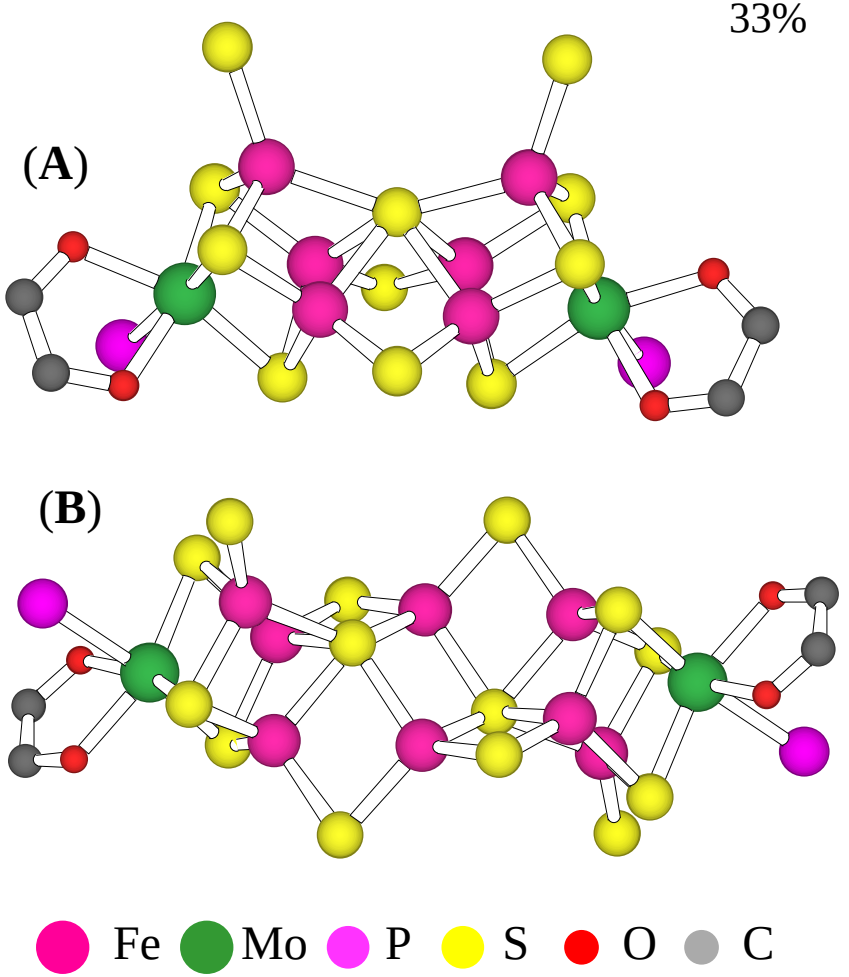
By R. H. Holm

F. Osterloh et al. *Angew. Chem. Int.Ed. Engl.* 1999, *38*, 2066

$$[Fe_3MoS_4(Cl_4cat)(PEt_3)]_2 \xrightarrow[CH_3NC]{2Et_4N(SH)} \xrightarrow[NMF]{Bu_4NPF_6} [Mo_6Fe_{20}S_{30}(Cl_4cat)_6(PEt_3)_6]^{8-}$$

33%





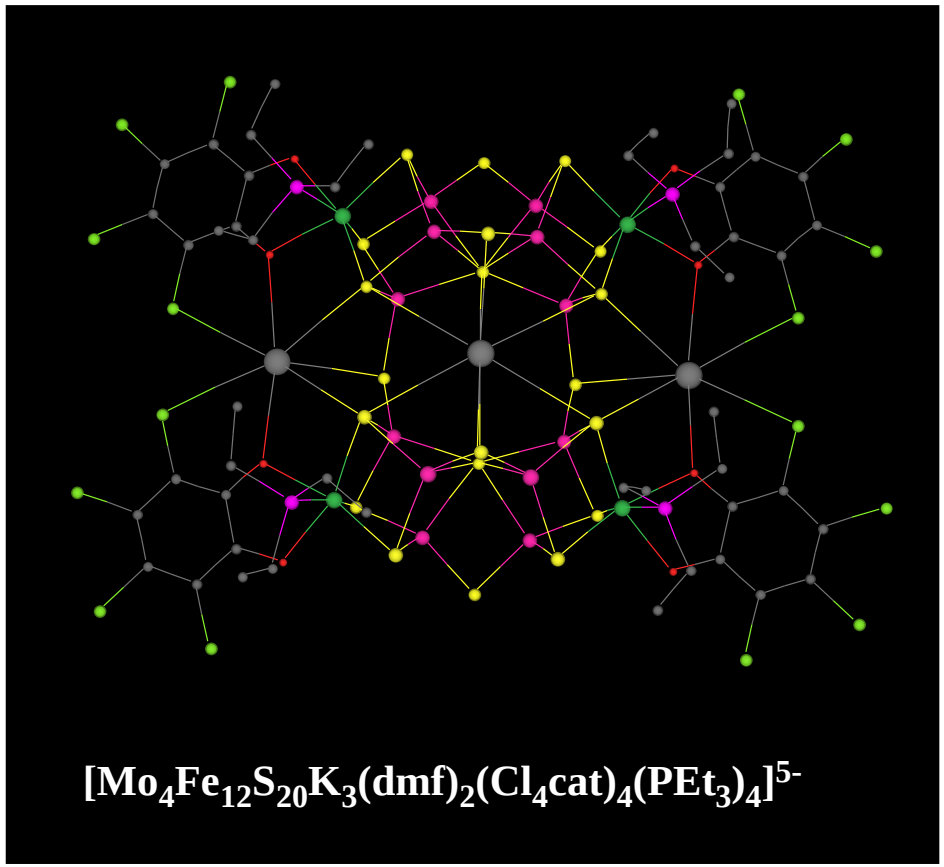
A Structural Model for P-Cluster of Nitrogenase

By R. H. Holm

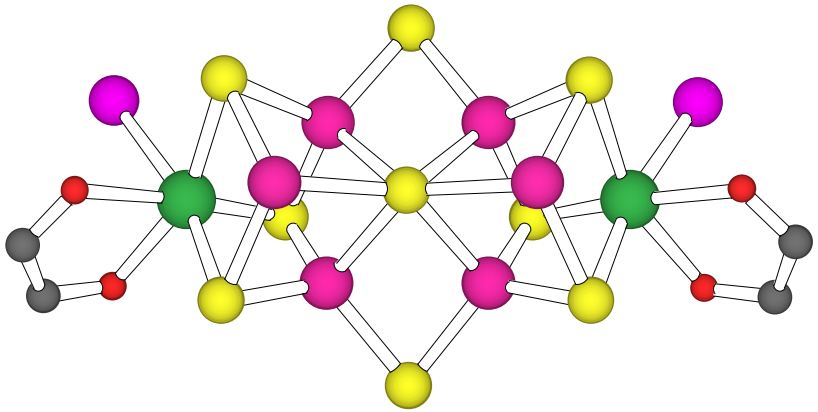
F. Osterloh et al. *Inorg. Chem.* 2001, *40*, 224

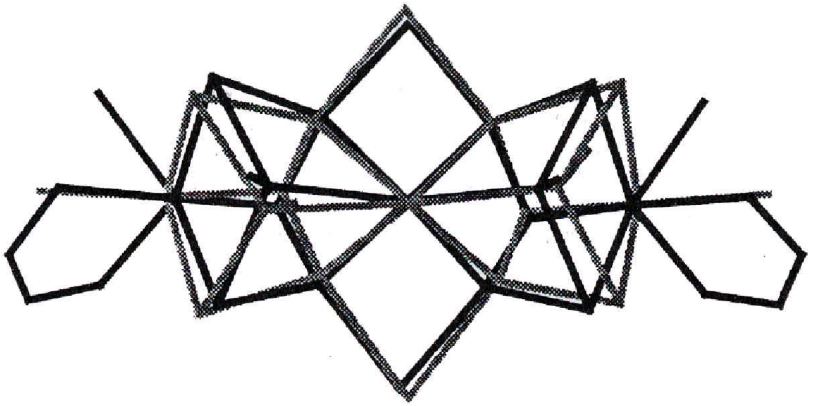
$$[Fe_3MoS_4(Cl_4cat)(PEt_3)]_2 \xrightarrow[THF/CH_3NC]{2Et_4N(SH)} \xrightarrow[DMF]{Ph_3MePBF_4} [Mo_4Fe_{12}S_{20}K_3(dmf)_2(Cl_4cat)_4(PEt_3)_4]^{5-}$$

25%



$[Mo_4Fe_{12}S_{20}K_3(dmf)_2(Cl_4cat)_4(PEt_3)_4]^{5-}$



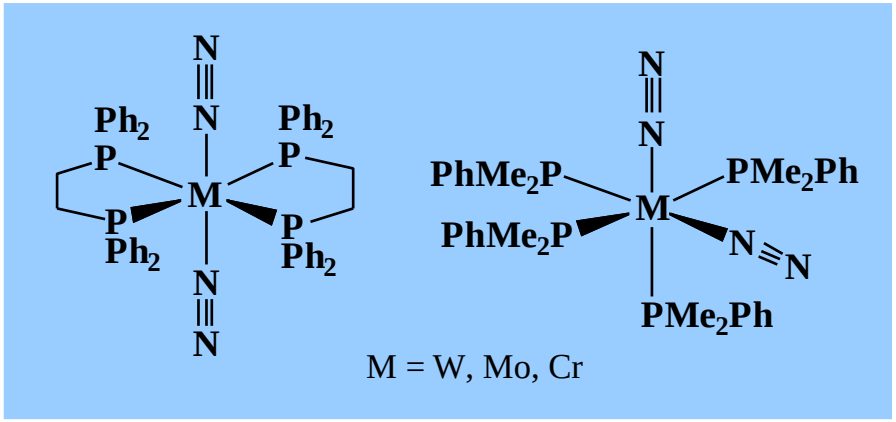


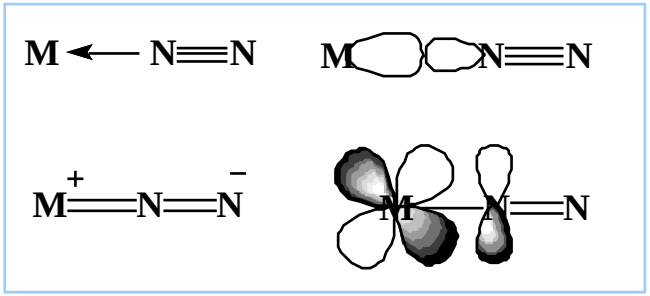
$Mo_2Fe_6S_9$ fragment P-cluster (P^N)

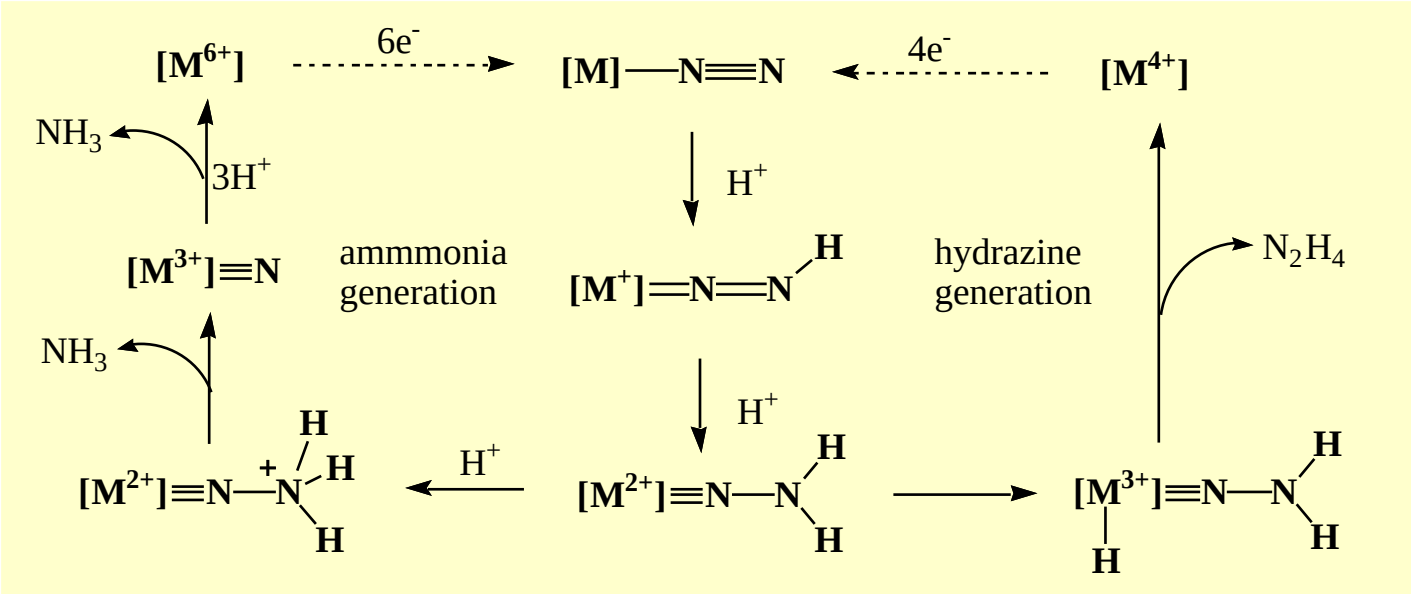
Functional Models for Nitrogenase

Dinitrogen Binding and Reduction Developed by Chatt and Hidai

Nature 1975
Chem. Rev. 1995







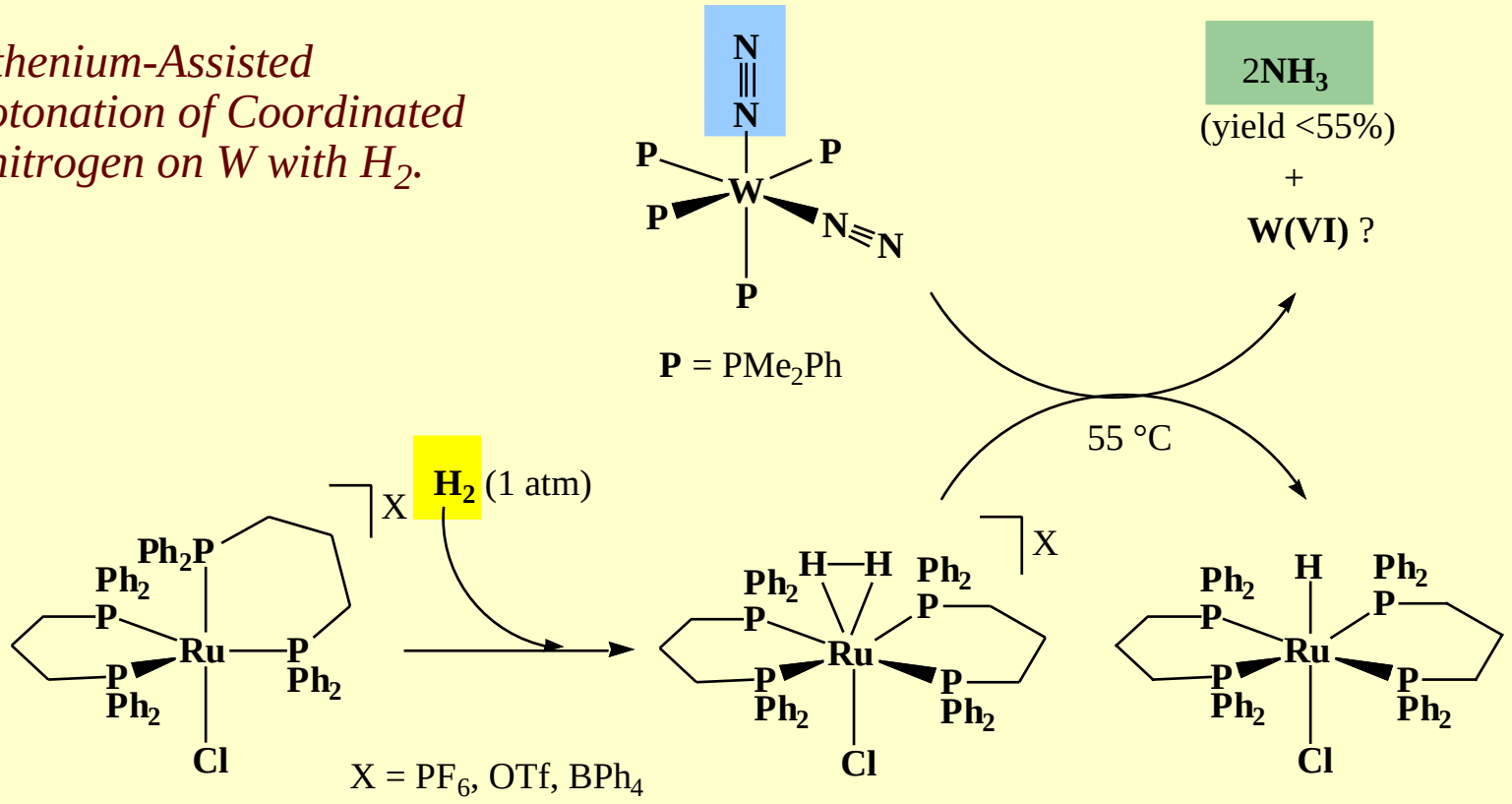
Chatt Cycle: Protonation of the coordinated dinitrogen

Not catalytic

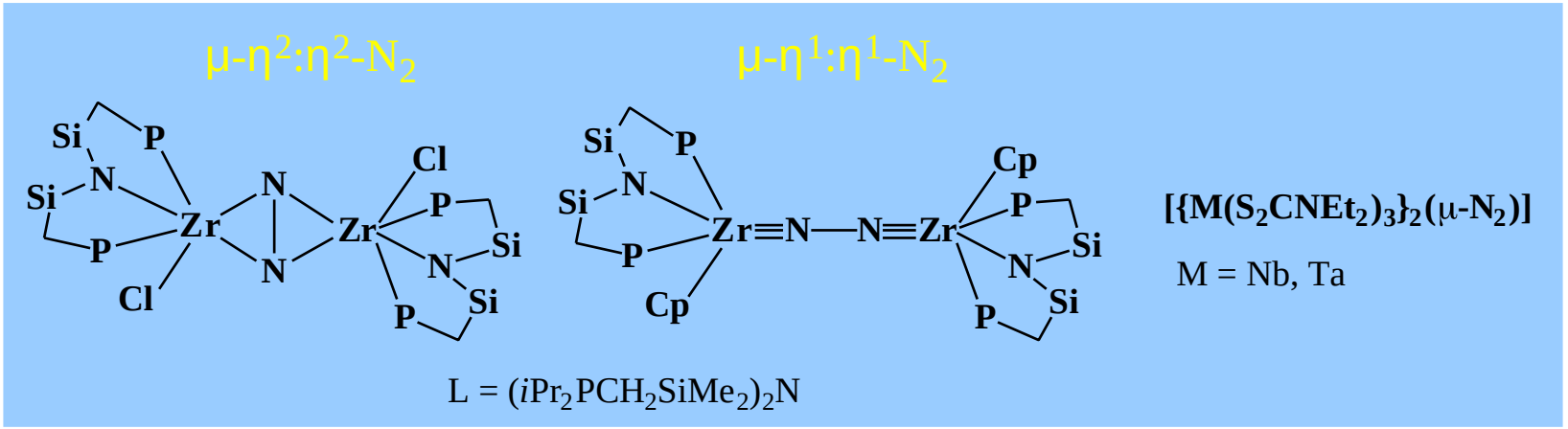
Bimetallic Functional Models for Nitrogenase

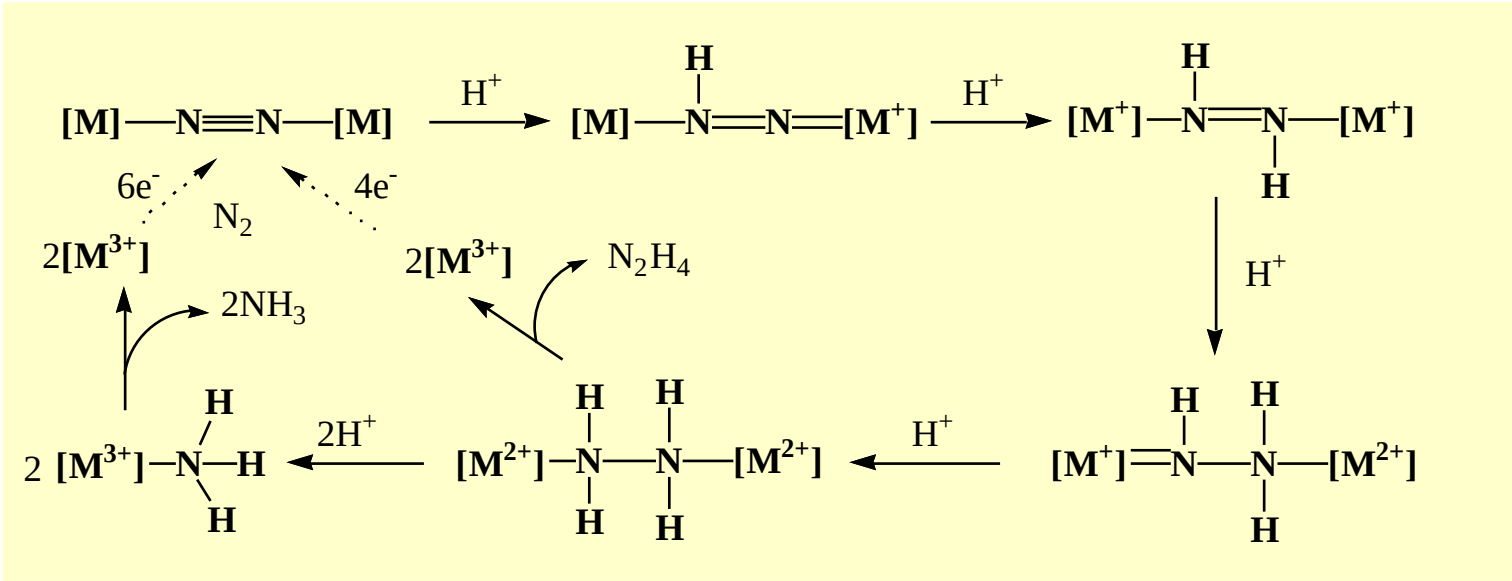
Y. Nishibayashi, S. Iwai, M. Hidai, *Science*, 1998, 279, 540

Ruthenium-Assisted Protonation of Coordinated Dinitrogen on W with H_2.



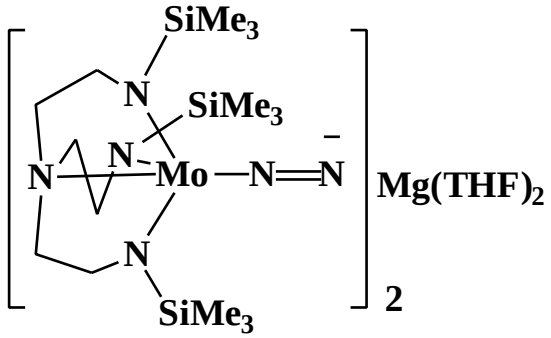
Protonolysis of Bridging Dinitrogen Ligands





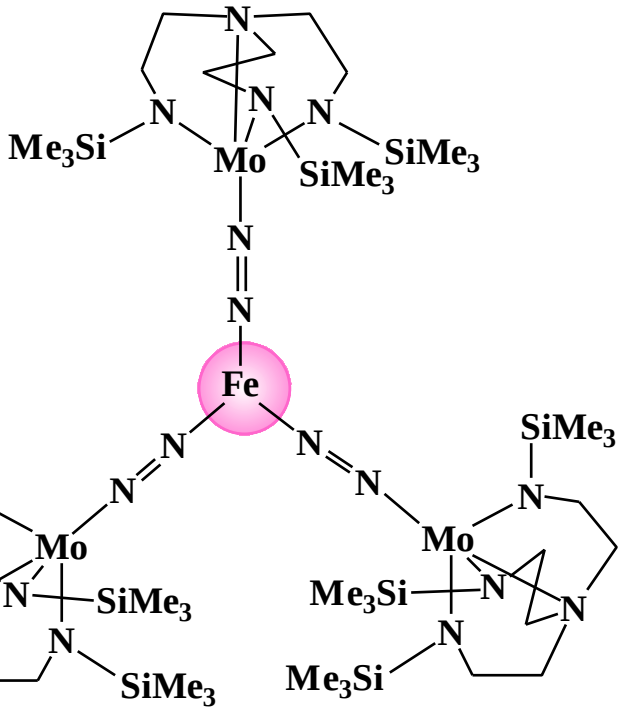
Not catalytic

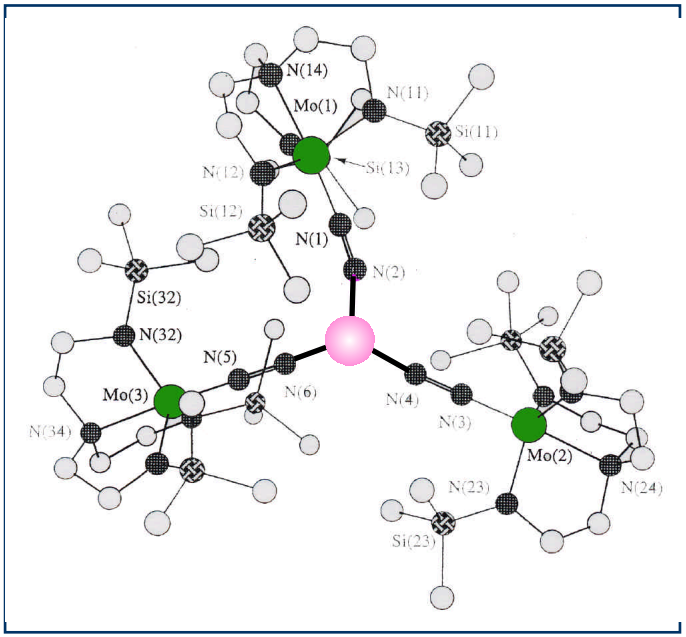
Bimetallic Dinitrogen Complex Containing Three Coordinate Iron Center



$FeCl_2$

-20 °C

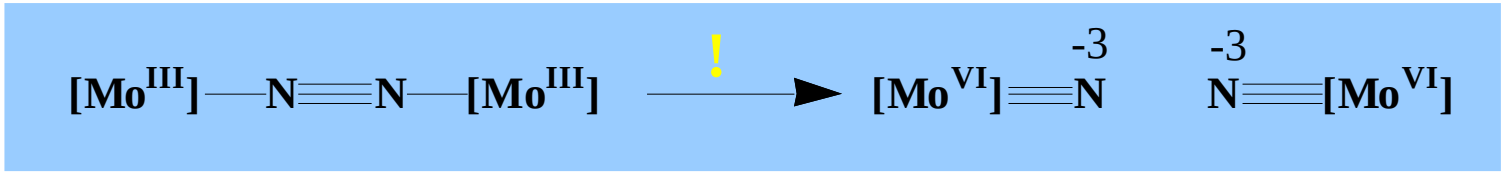




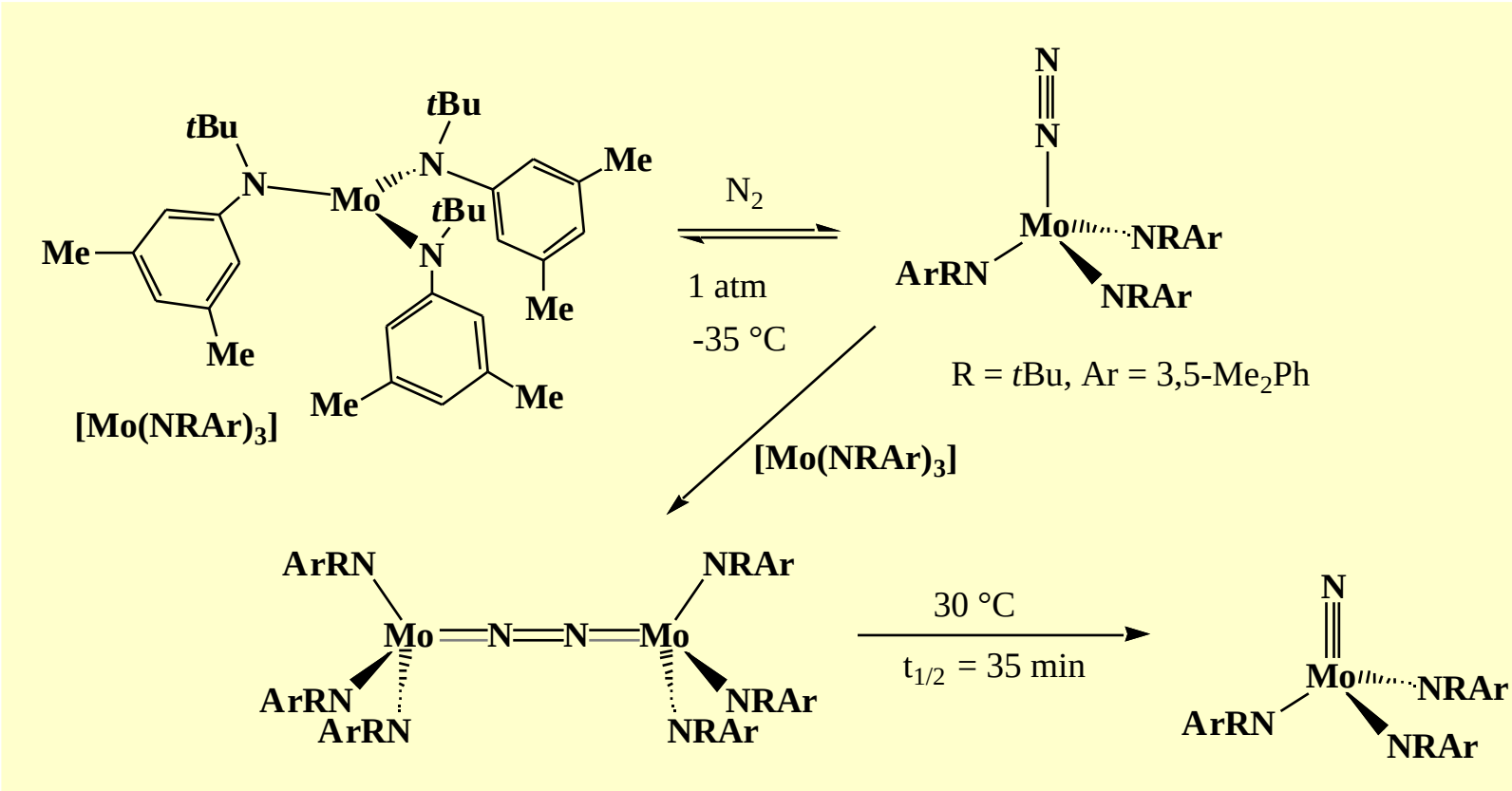
three coordinate Fe(III) center
high spin

R. R. Schrock et al. *Inorg. Chem.* 1999, *38*, 243

Dinitrogen Cleavage by a Three-Coordinate Molybdenum(III) Complex

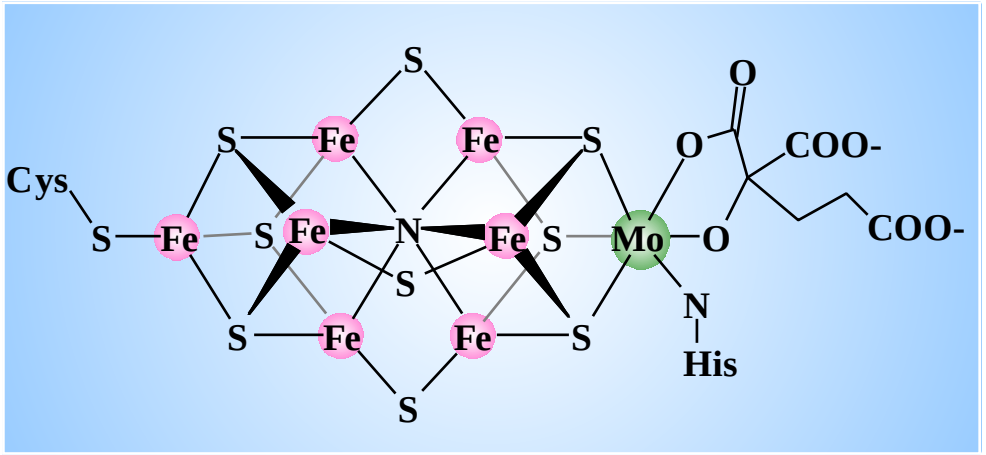


C. E. Laplaza, C. C. Cummins, *Science* 1995, *268*, 861



Think Again Haber-Bosch Reaction in Relation to Nitrogenase

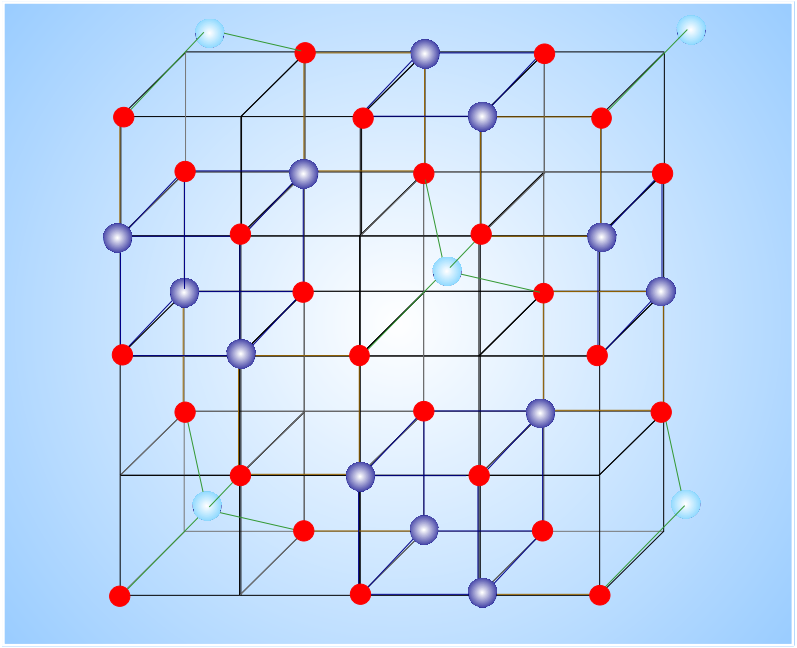
Nitrogenase



FeMo cofactor (Active Site)

Structural + Functional Model?

Haber-Bosch



Magnetite Fe_3O_4 (Catalyst)

AB_2O_4 Spinel Structure

A B O

A = Fe(III), B = Fe(II)Fe(III)

Thanks for Your Attention!!

1) **2002** *Nara Women's University*
2)
3)