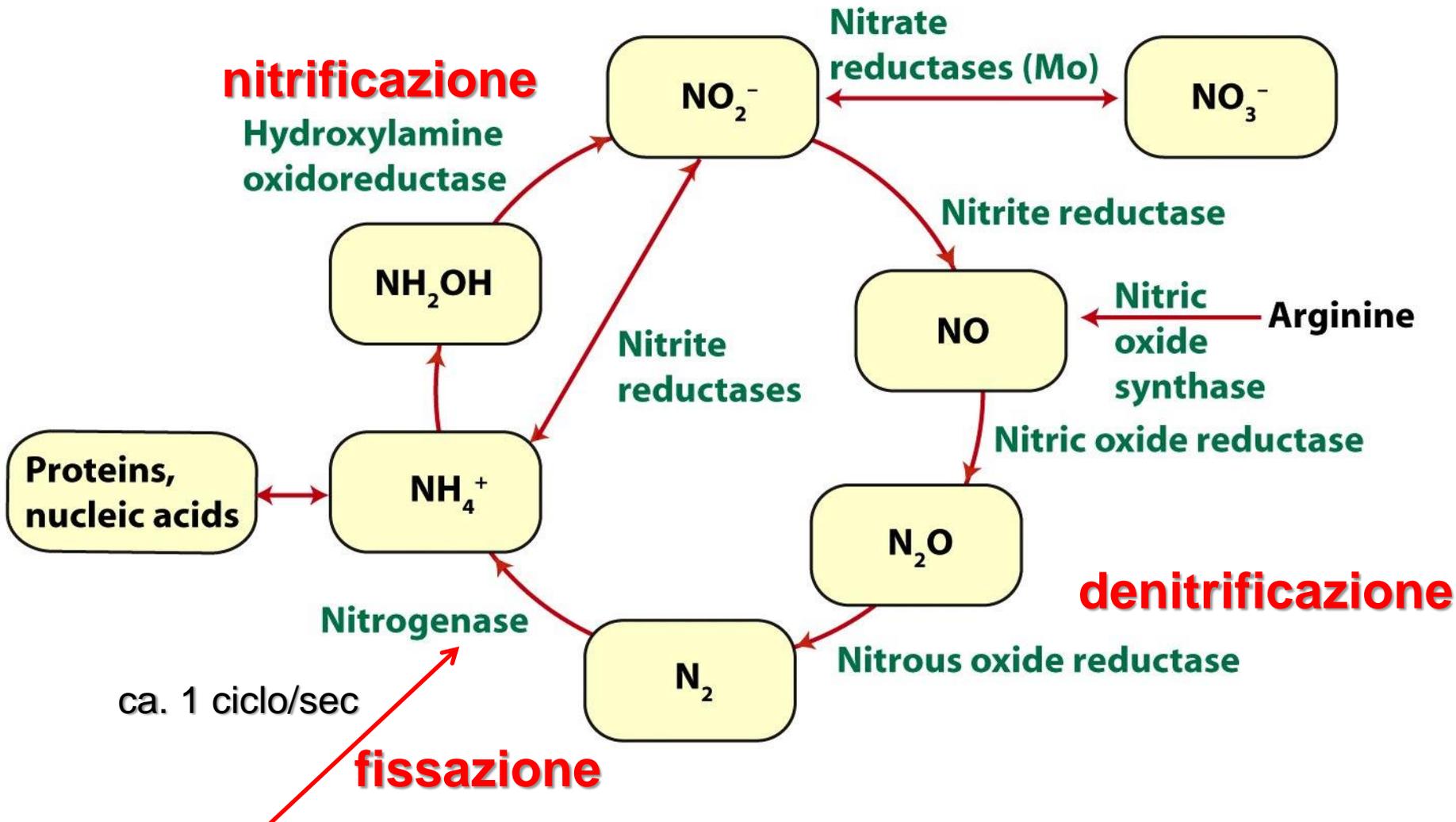


# Metalli di inizio serie

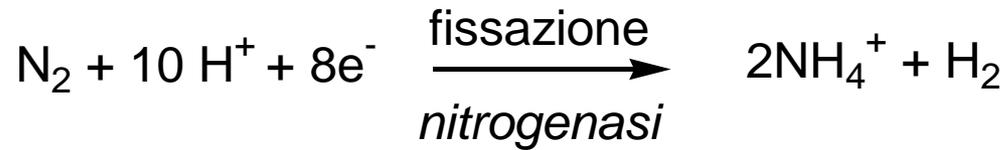
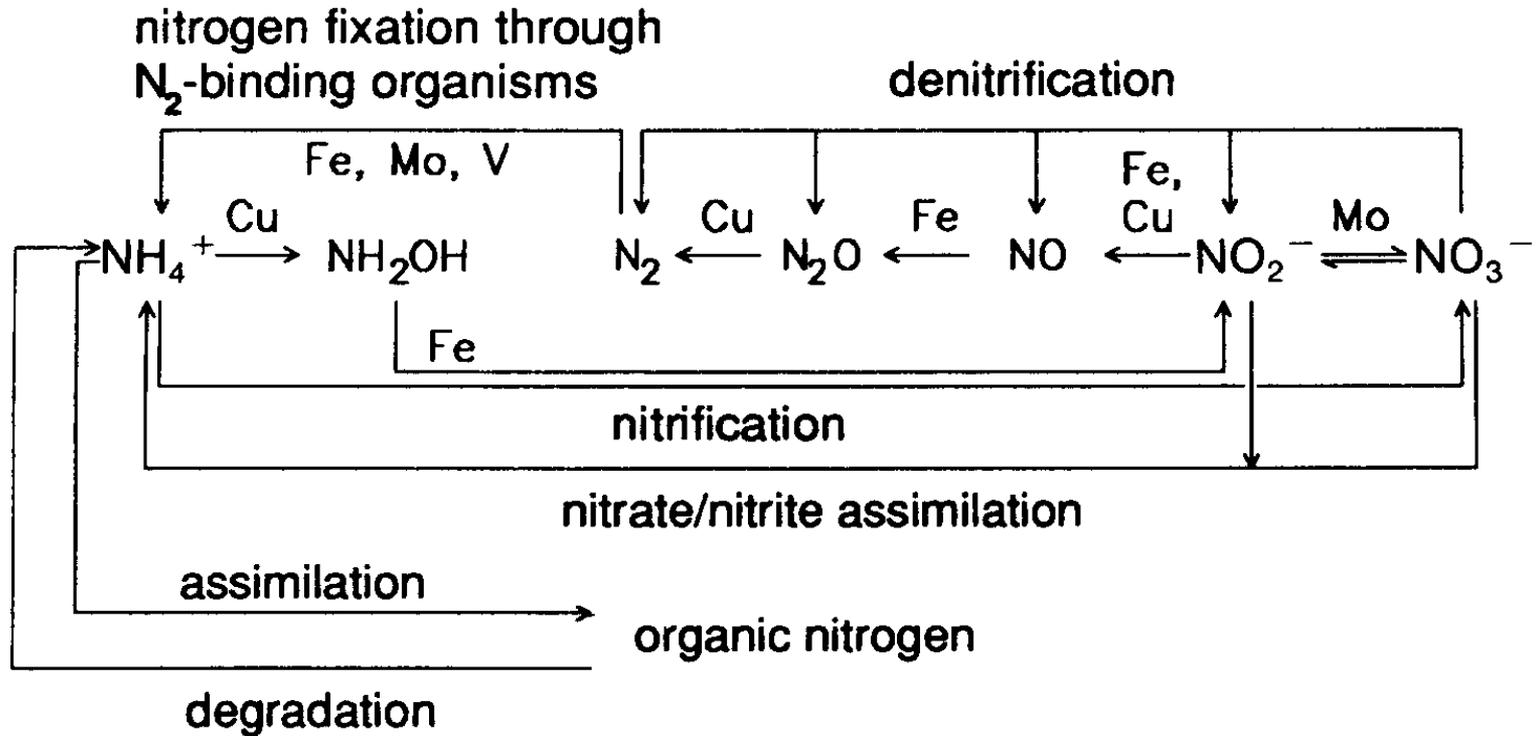


*Il molibdeno è l'unico elemento del secondo periodo di transizione (4d) ad avere una funzione biologica*

# Ciclo dell'azoto



Batteri procarioti diazotropici (leguminose): 10<sup>8</sup> ton N<sub>2</sub>/y

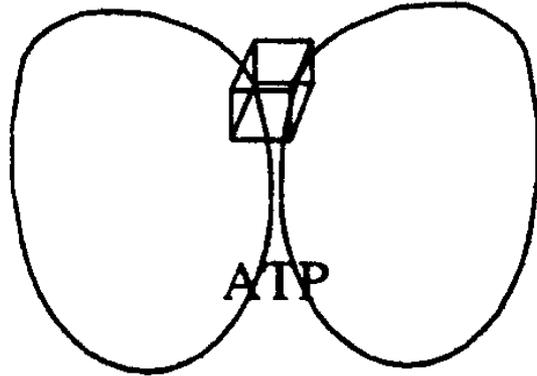


# Nitrogenasi



1992

ca. 1 ciclo/sec

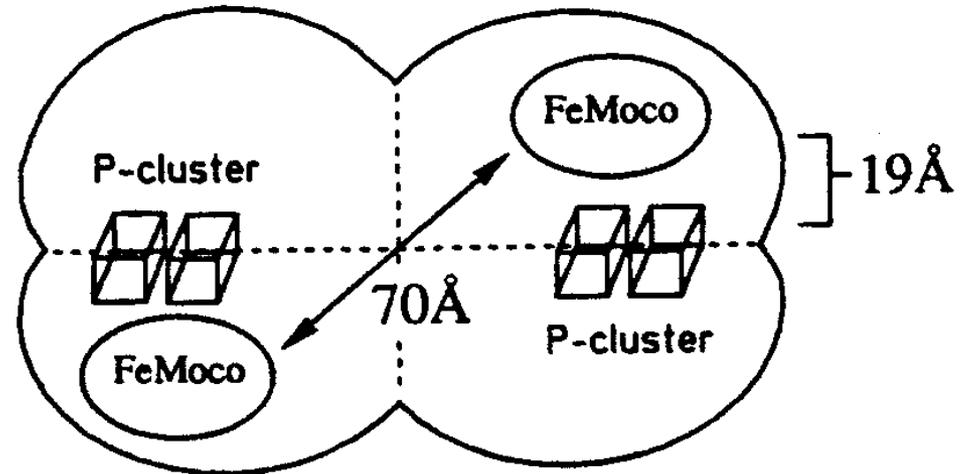


**Fe protein**

$\gamma_2$

60 kDa

+



**FeMo protein**

$\alpha_2\beta_2$

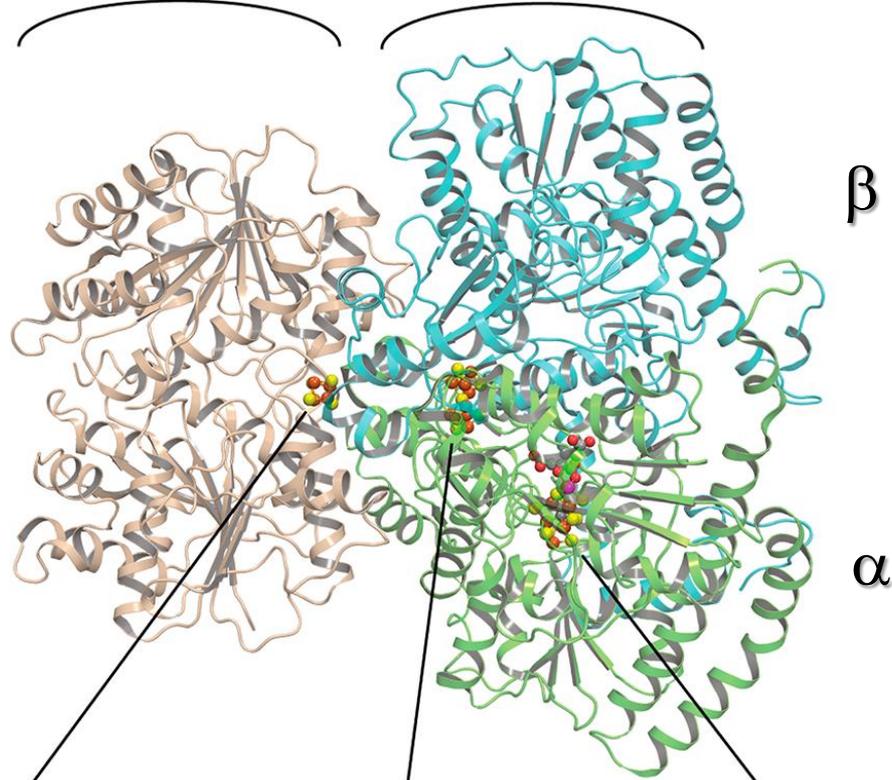
220 kDa

# Nitrogenasi

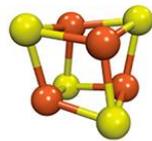
Fe protein

MoFe protein

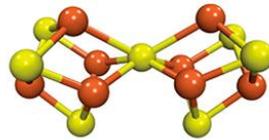
(A)



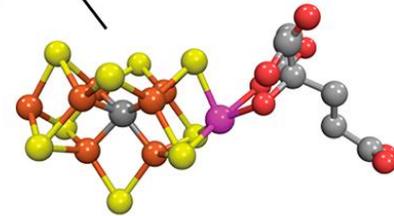
(B)



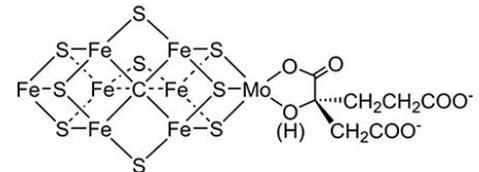
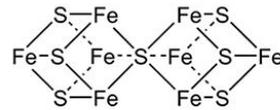
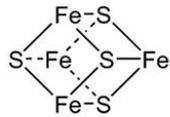
F cluster



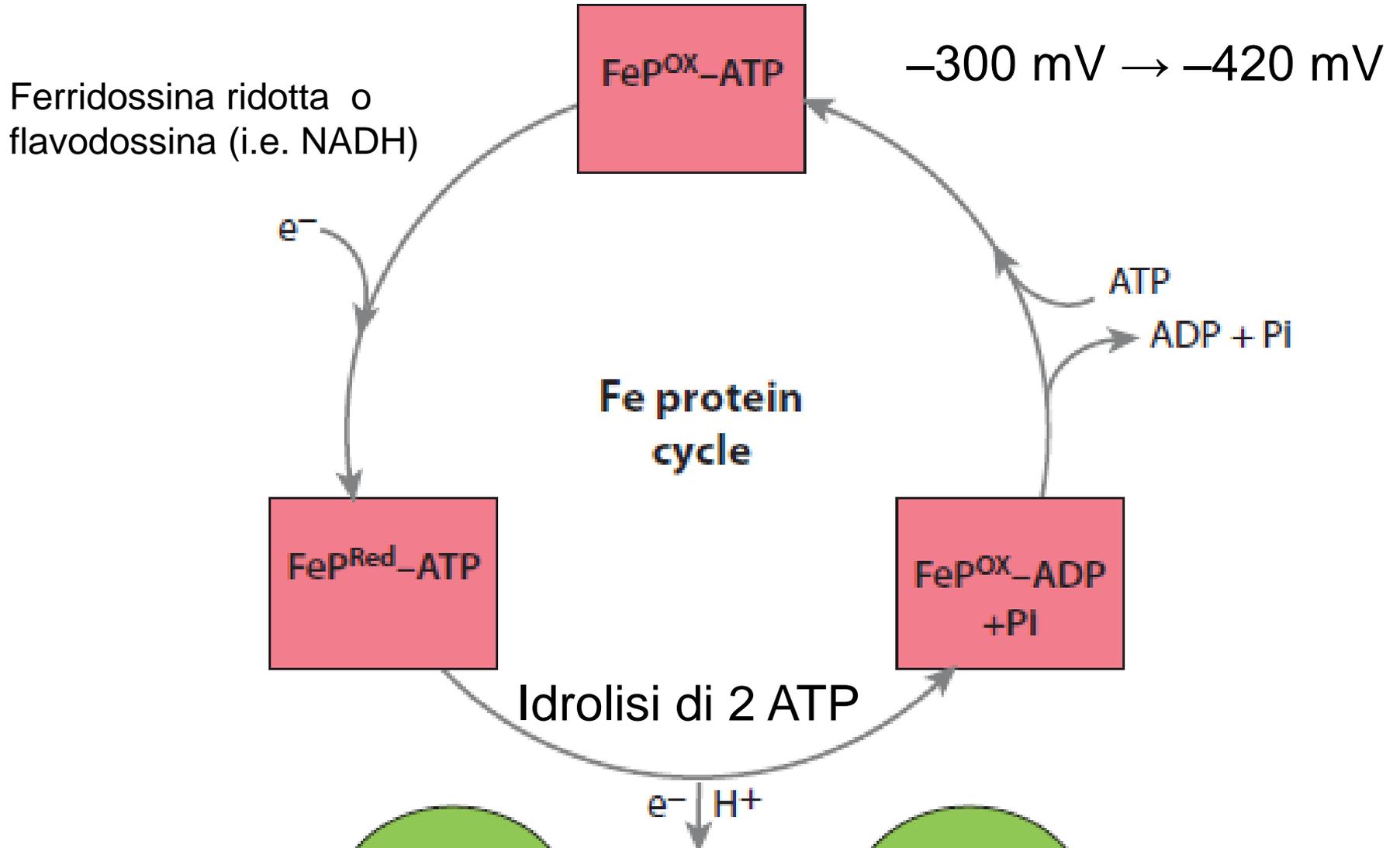
P cluster



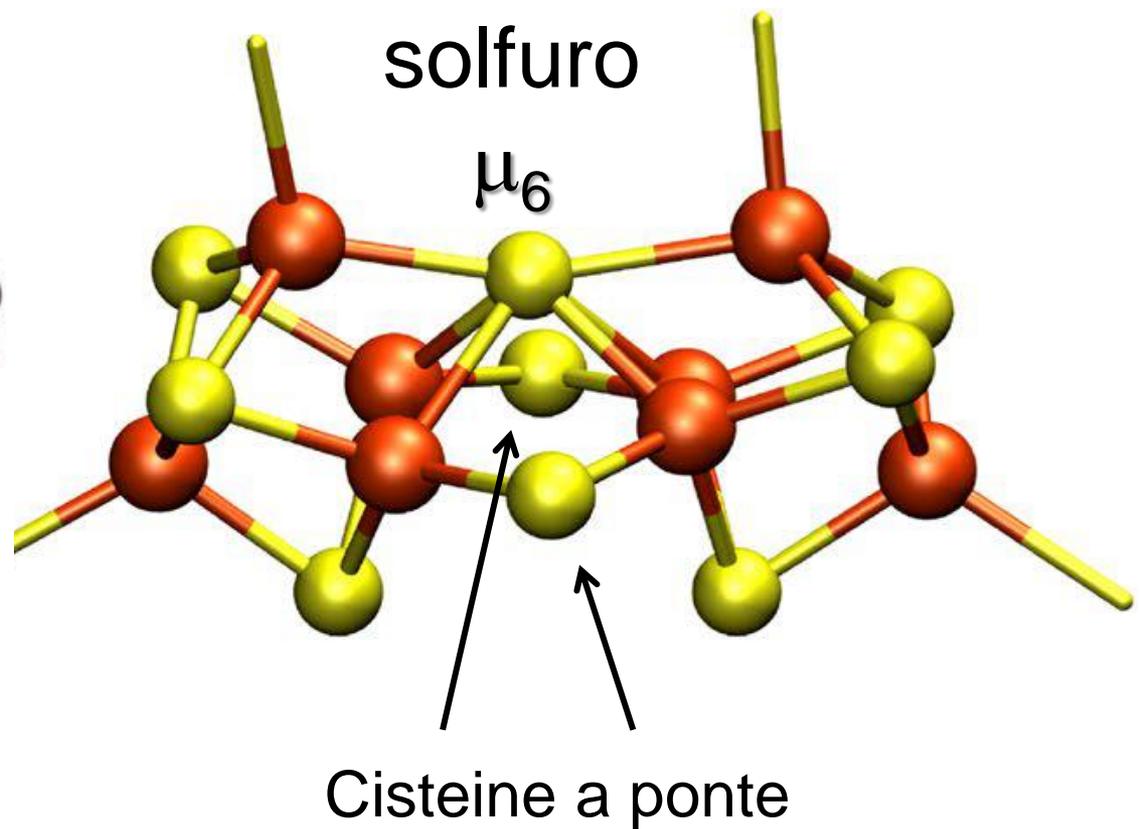
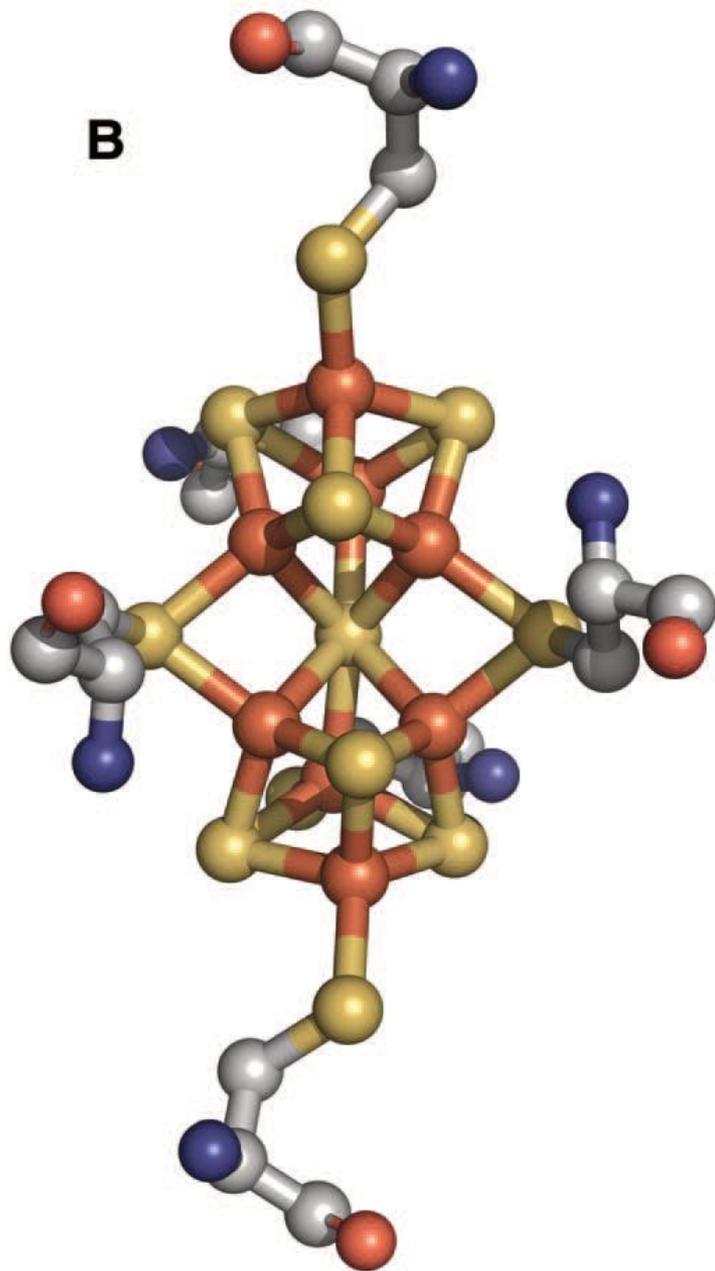
M cluster (FeMoco)



# Fe-proteina

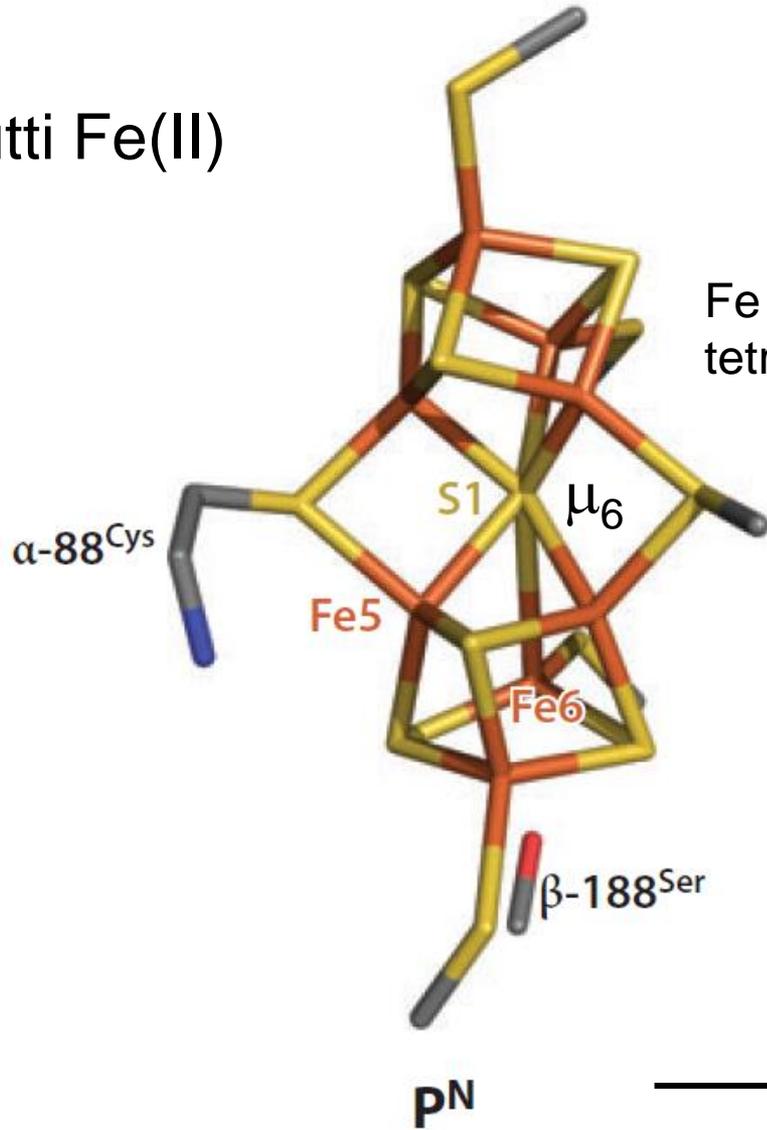


# P-cluster 8Fe-7S



# P-cluster 8Fe-7S

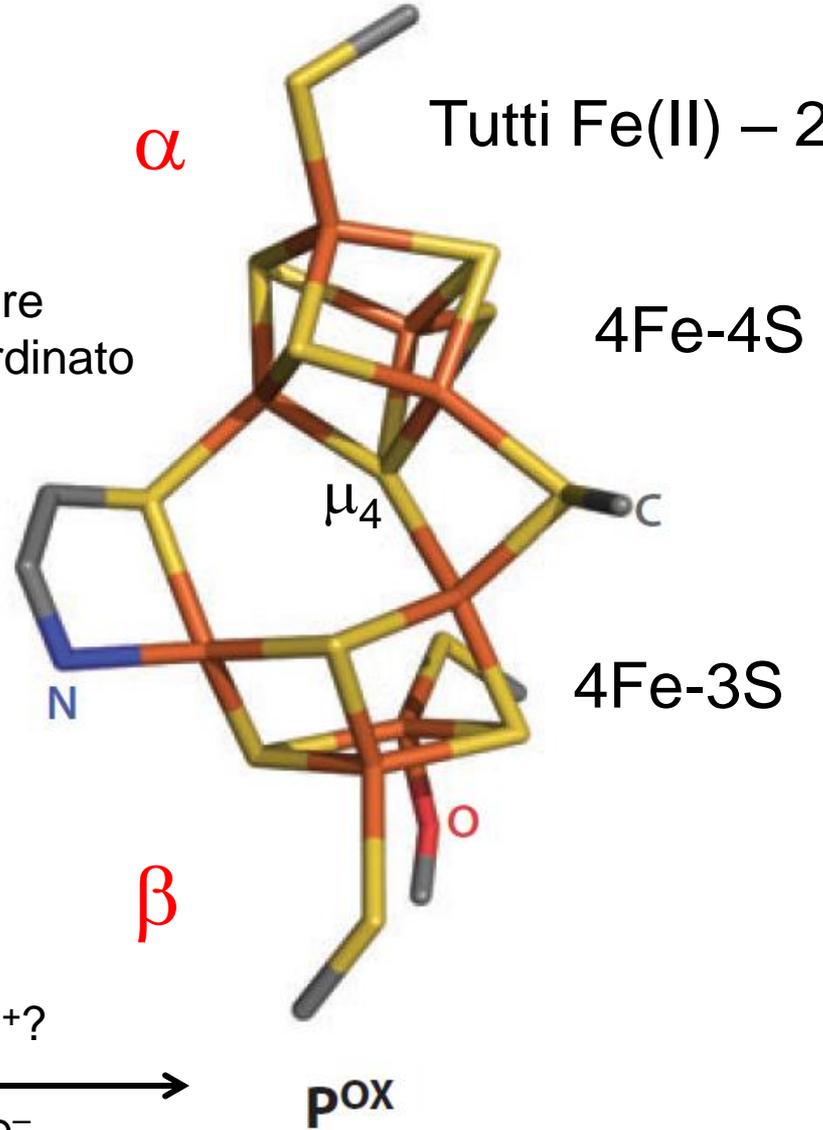
Tutti Fe(II)



Fe sempre  
tetracoordinato

$\alpha$

Tutti Fe(II) – 2e<sup>-</sup>



4Fe-4S

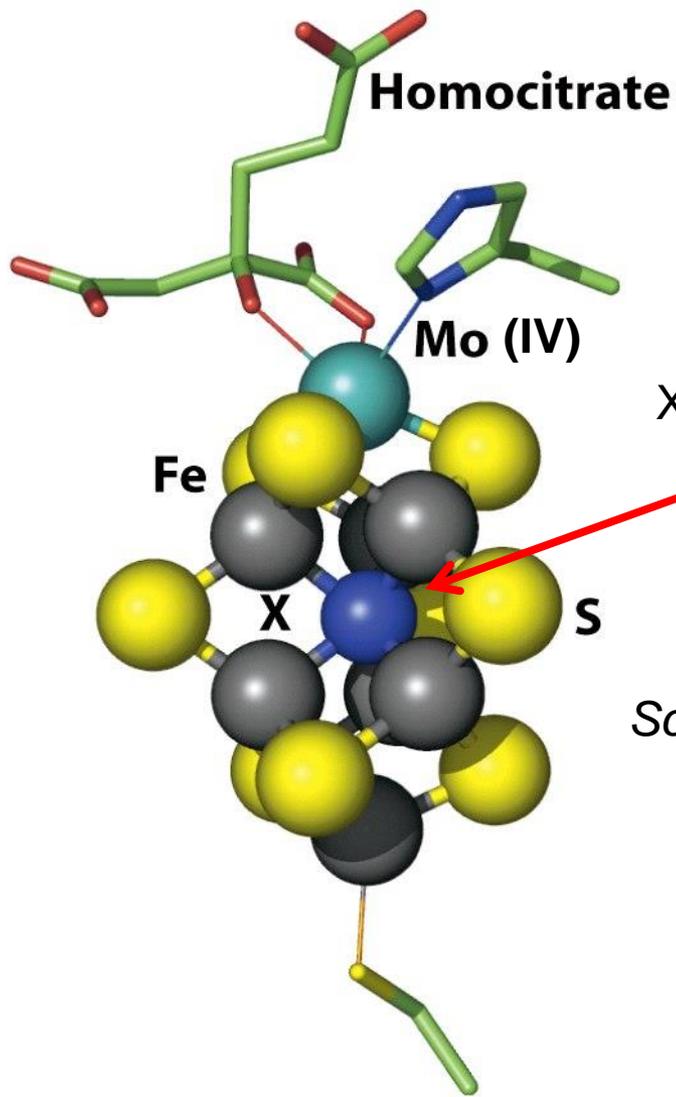
4Fe-3S

$\beta$

-2H<sup>+</sup>?

-2e<sup>-</sup>

POX



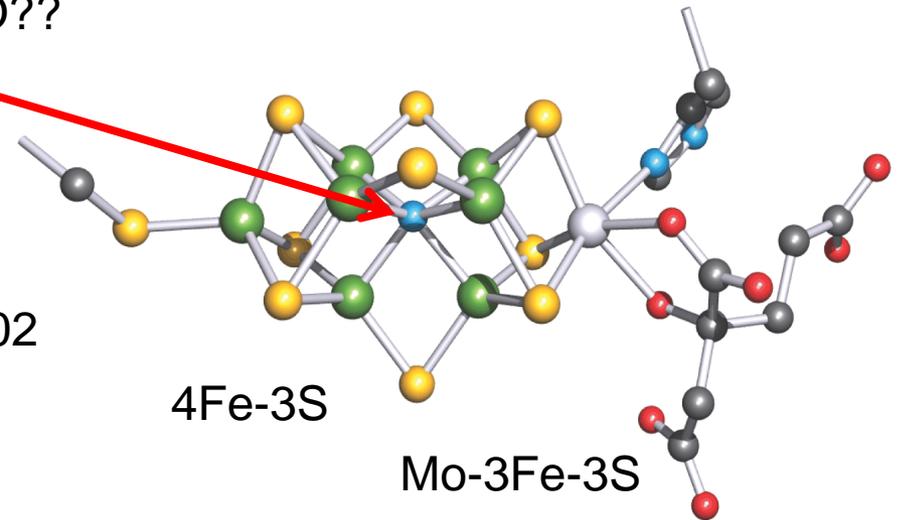
**Nitrogenase FeMoCo**

# Cofattore FeMo

## 7Fe-9S-Mo-omocitrato

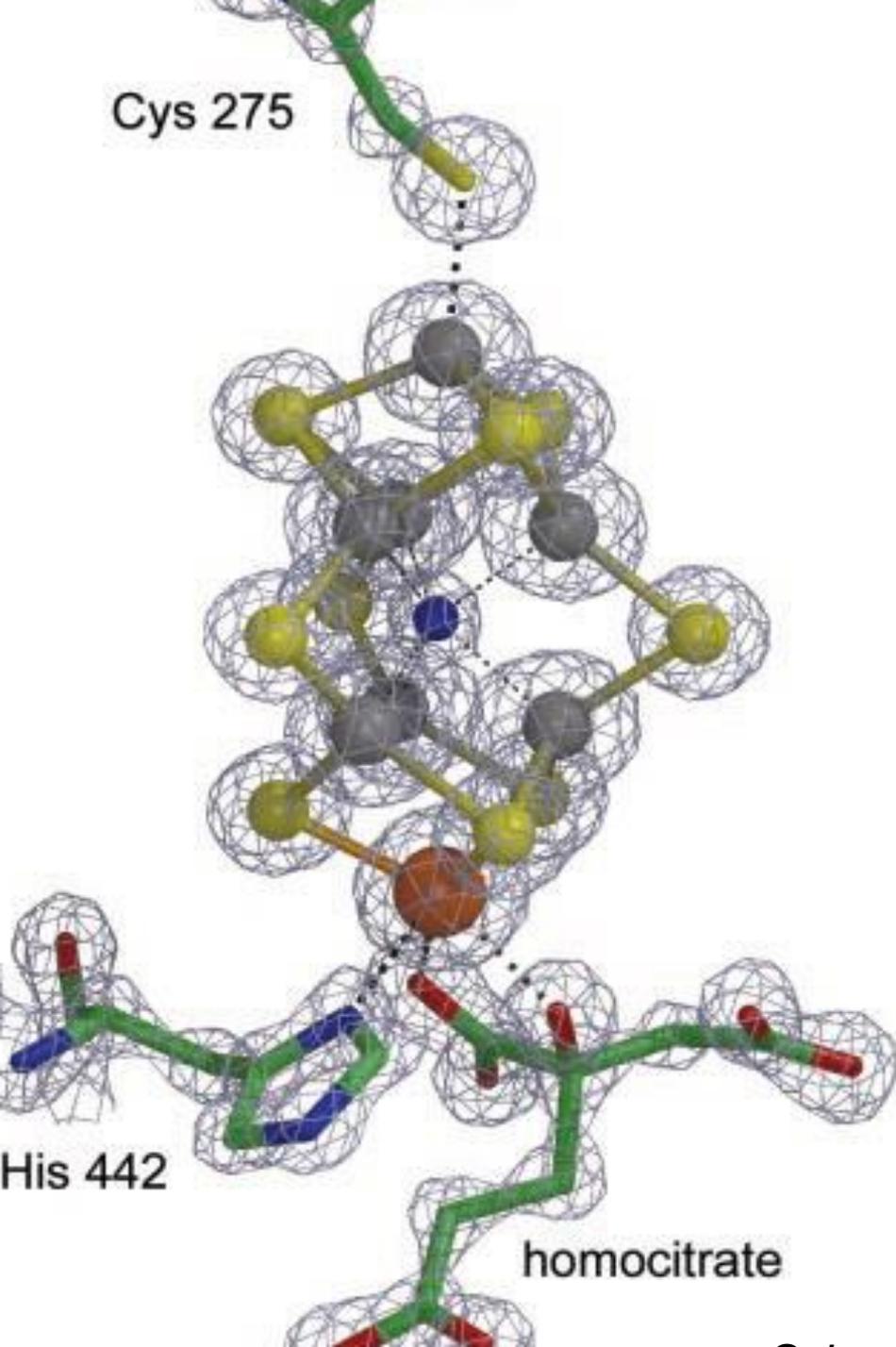
X = C, N, O??

*Science*, 2002

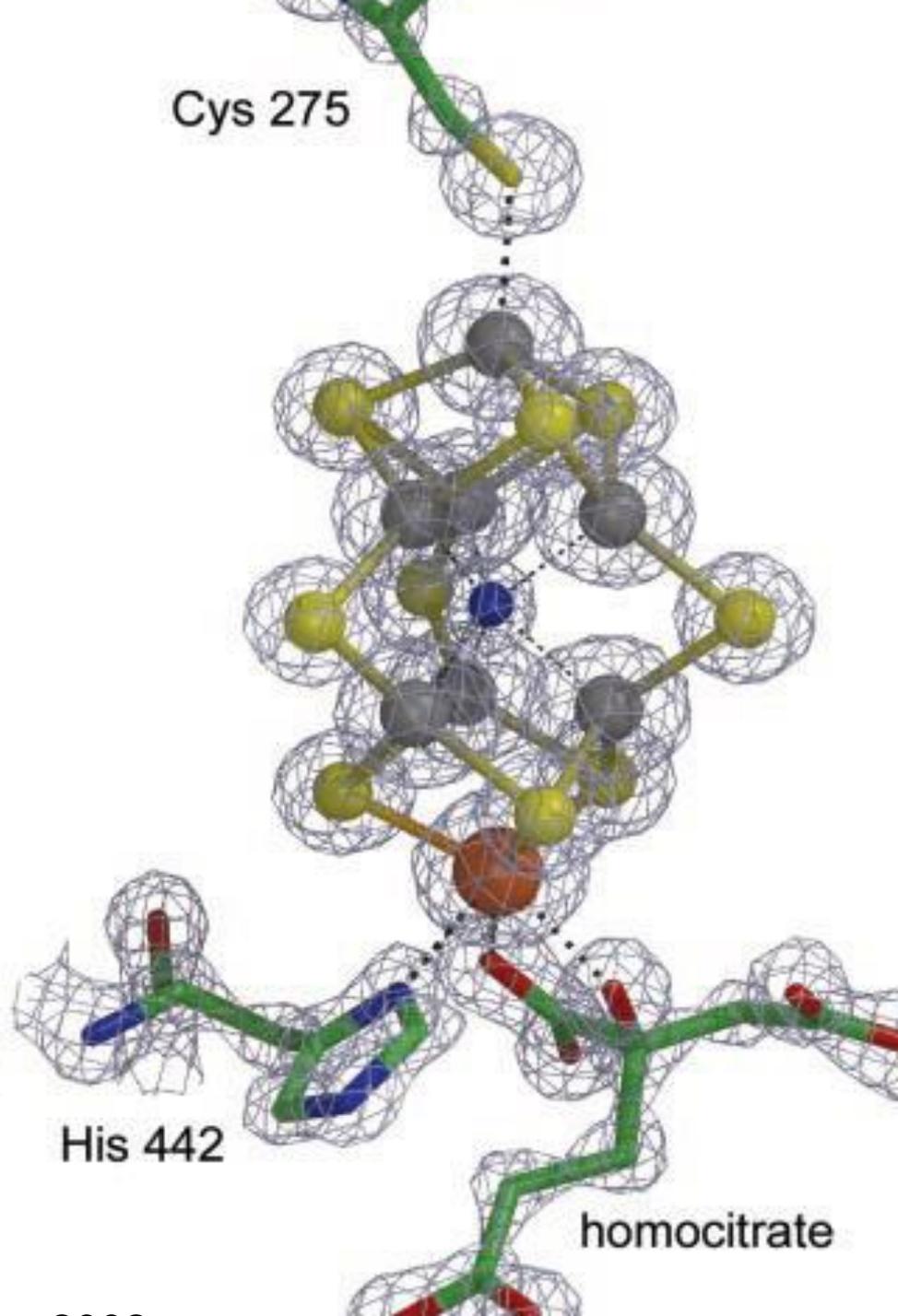


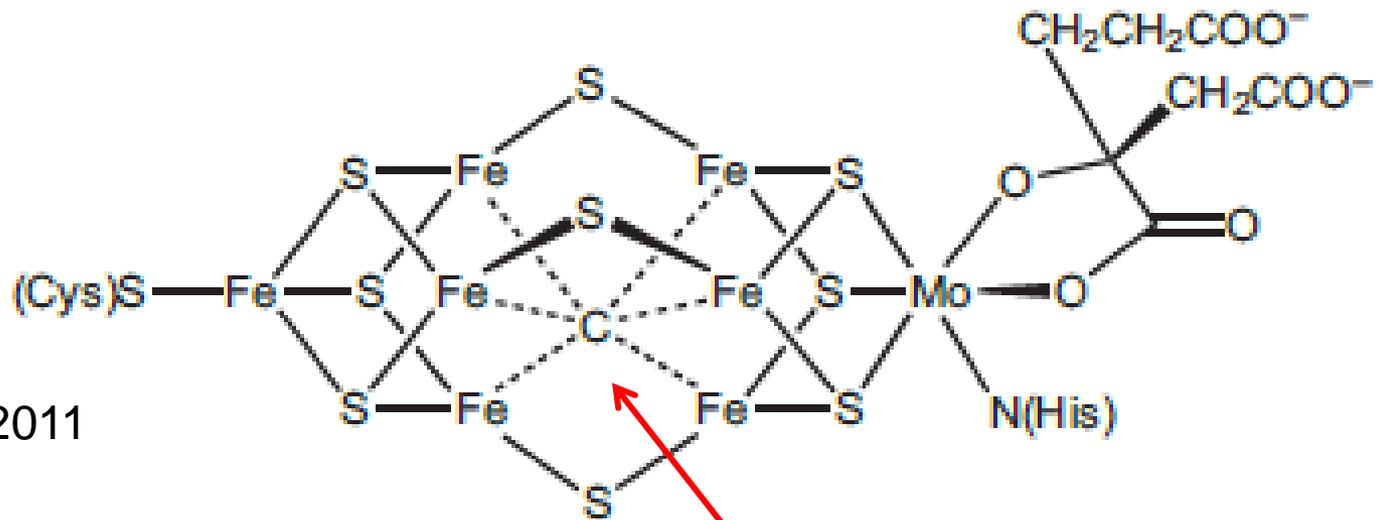
Tutto in  $\alpha$

Cys 275



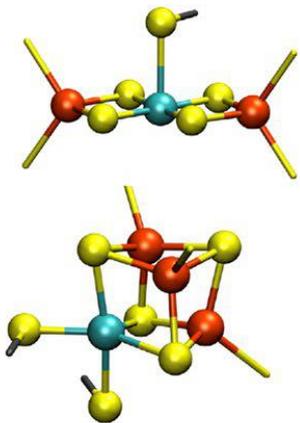
Cys 275





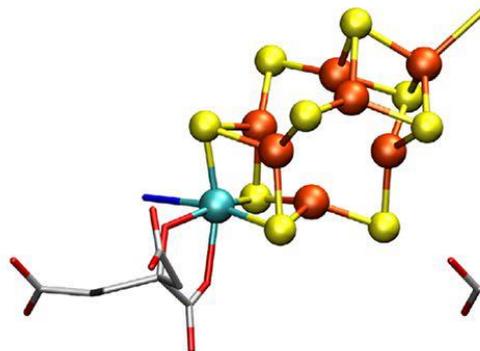
*Science*, 2011

Carburo, C<sup>4-</sup>



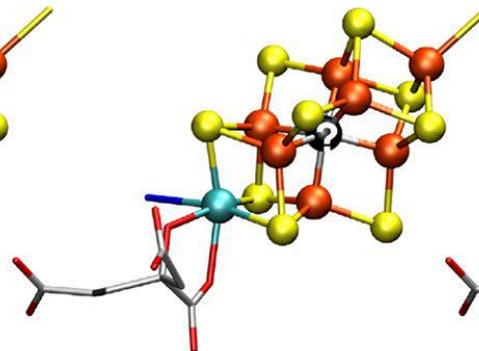
1978

First structural models from EXAFS



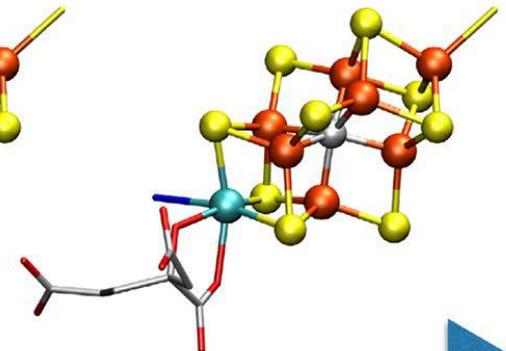
1992

First crystal structure (2.7Å)



2002

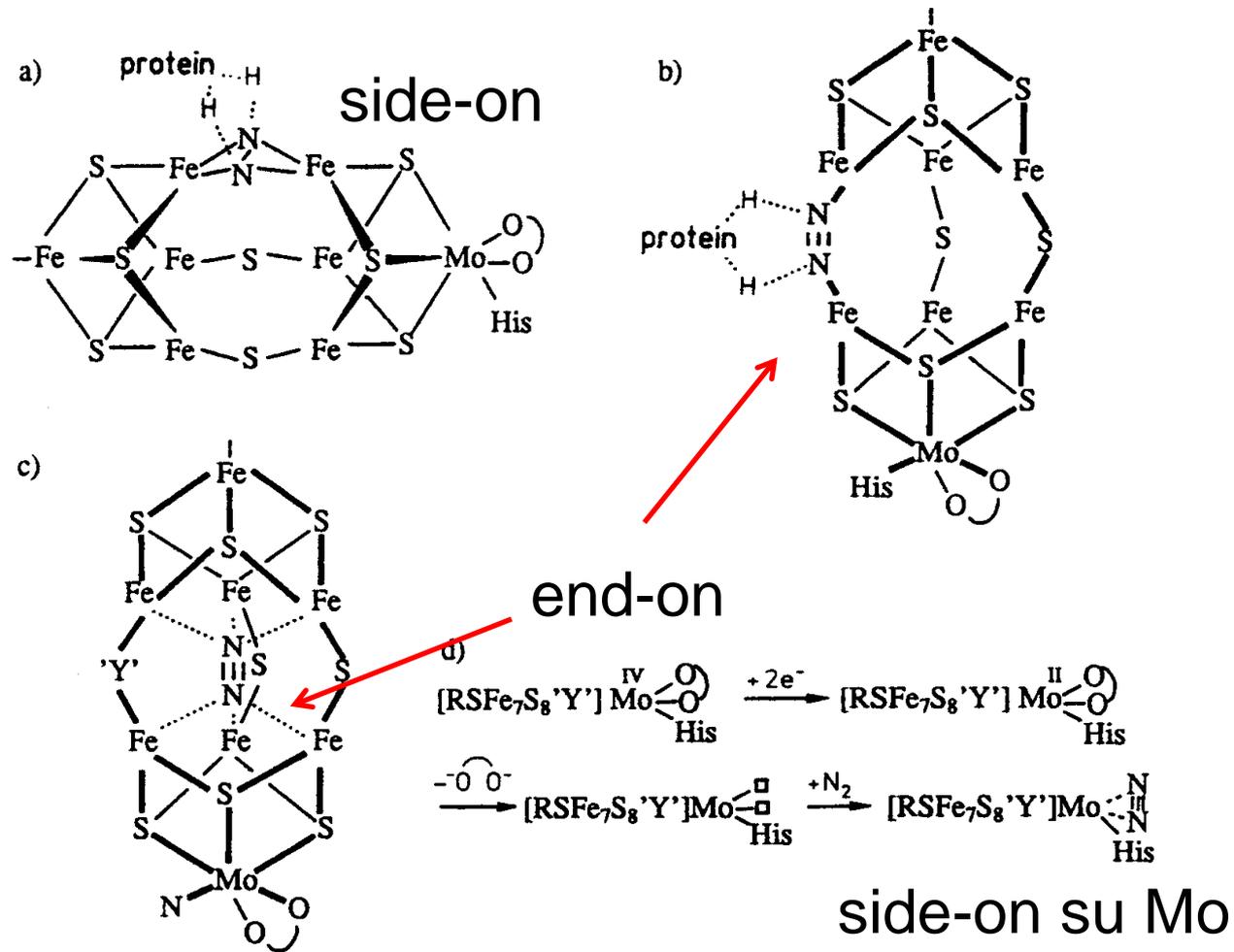
Discovery of interstitial atom



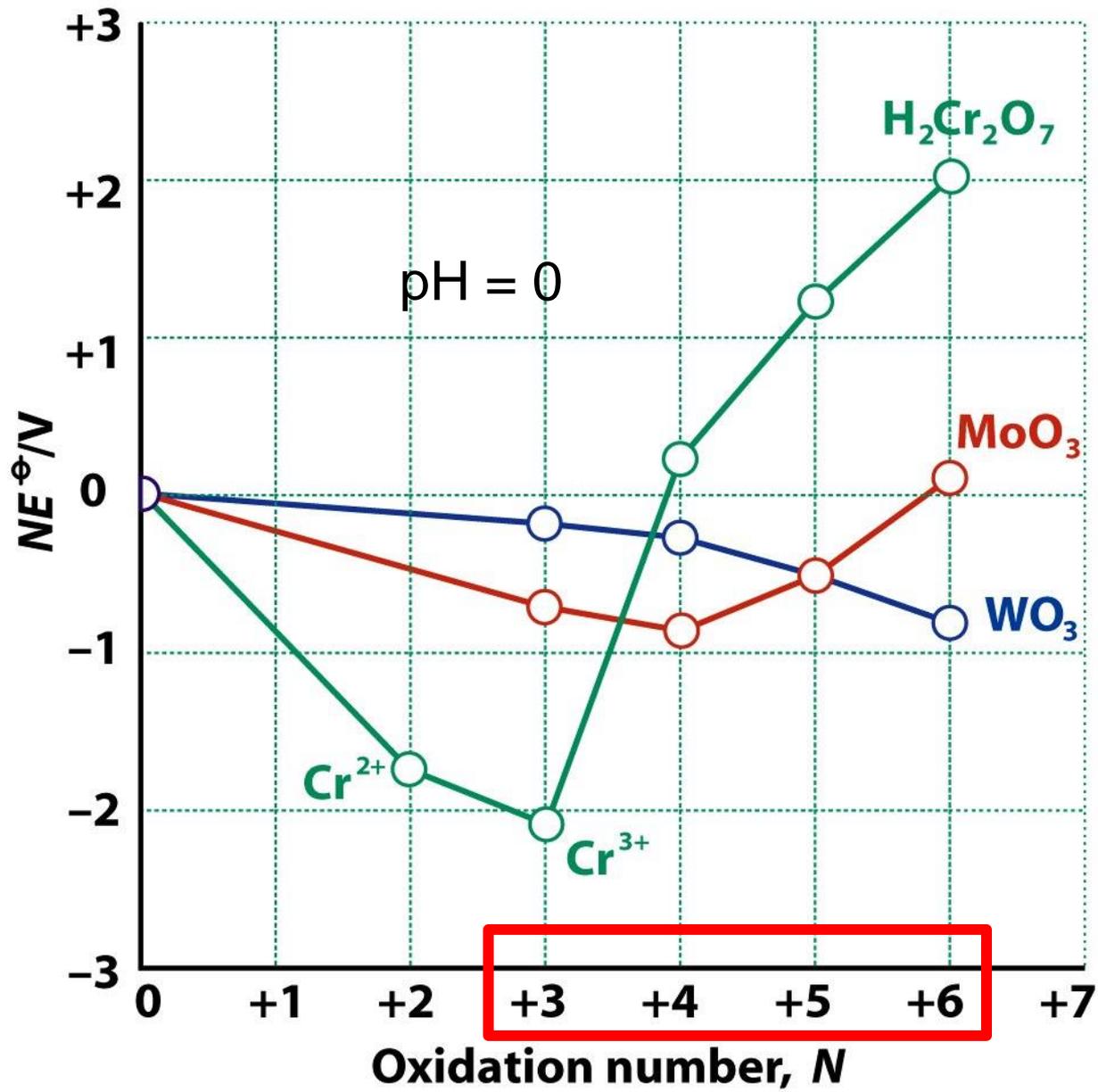
2011

Interstitial atom identified as carbon

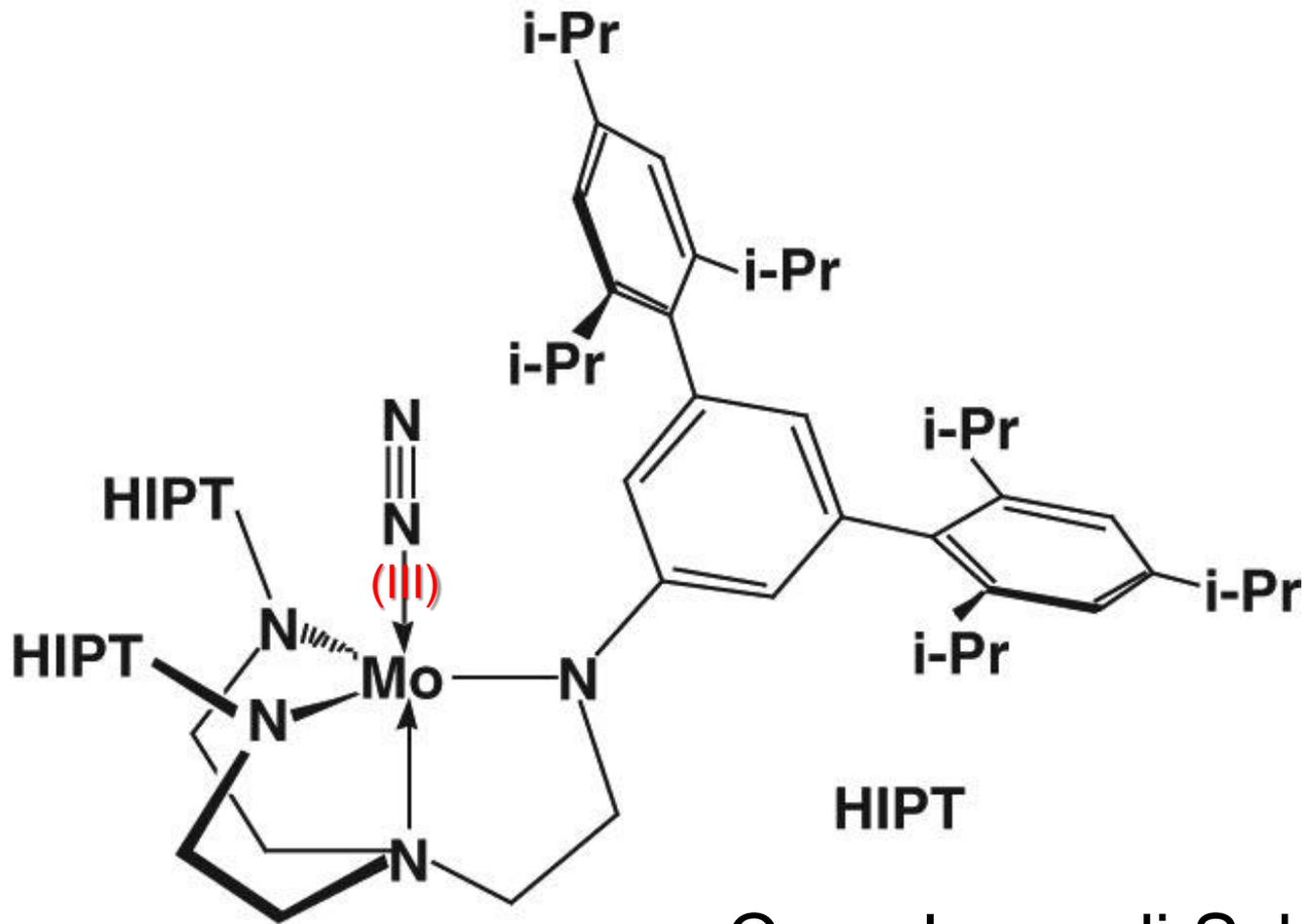
# Ipotetici modi di coordinazione di N<sub>2</sub> al FeMoco



*FeMo-co coordina N<sub>2</sub> solo dopo essere stato ridotto con 4 elettroni*

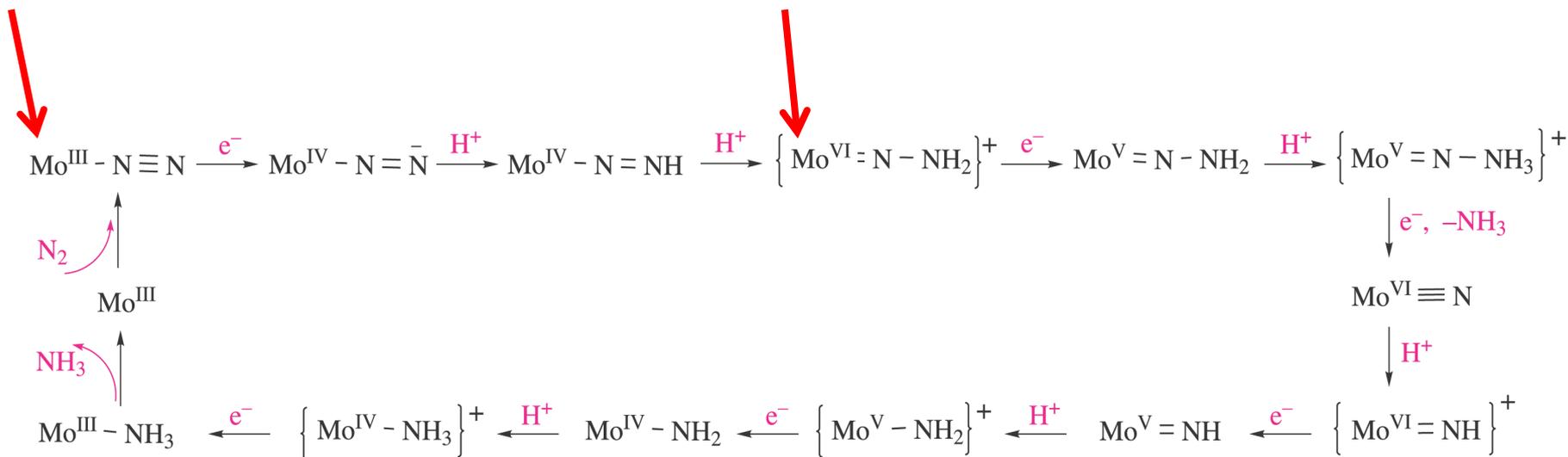
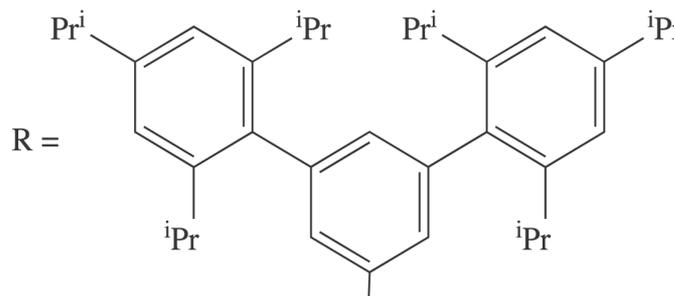
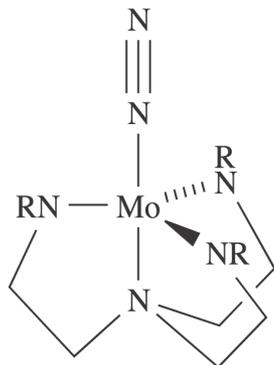


# Modelli



Complesso di Schrock  
(*Science* 2003)

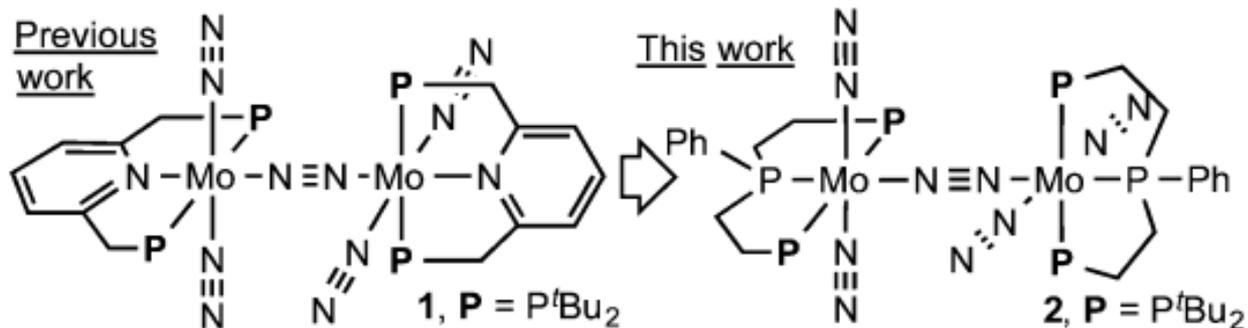
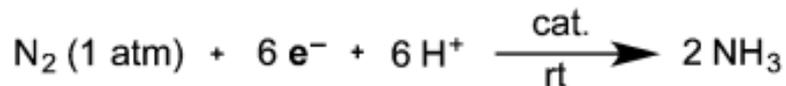
# Schema della riduzione catalitica di N<sub>2</sub> a NH<sub>3</sub> su Mo



8 cicli catalitici, meccanismo *distale*

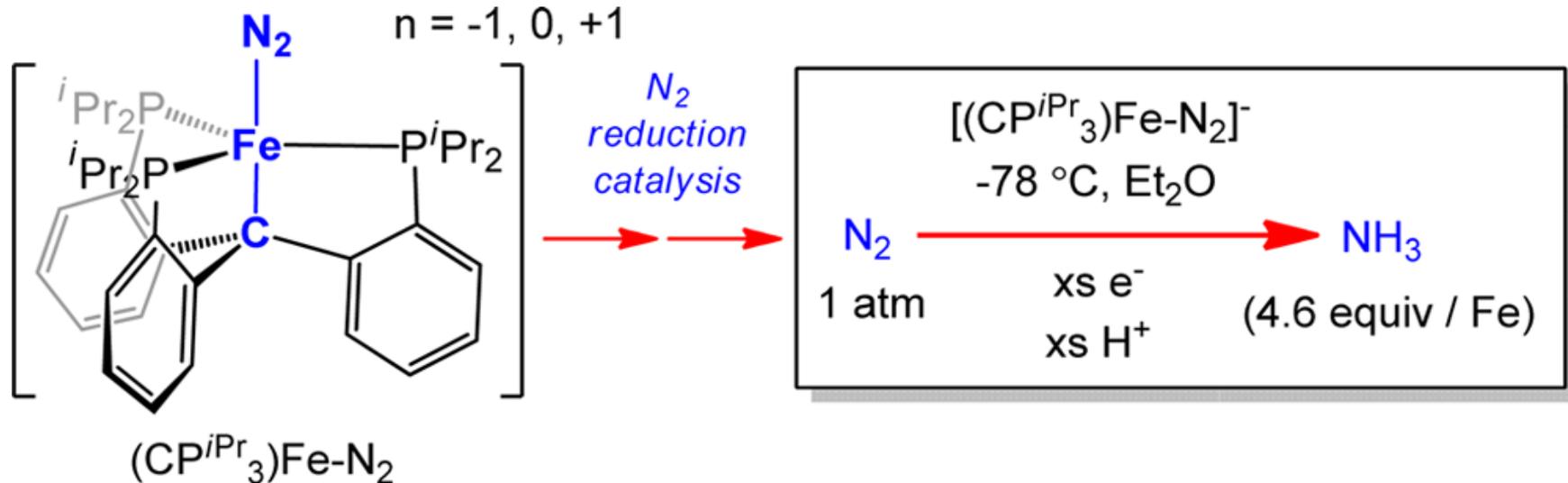
# Complessi di Nishibayashi (2011 e 2015)

## 26 cicli catalitici, riducente $\text{CoCp}^*_2$



# Complesso di Peters (2014)

## 4.6 cicli catalitici, riducente $\text{K}(\text{crown})$



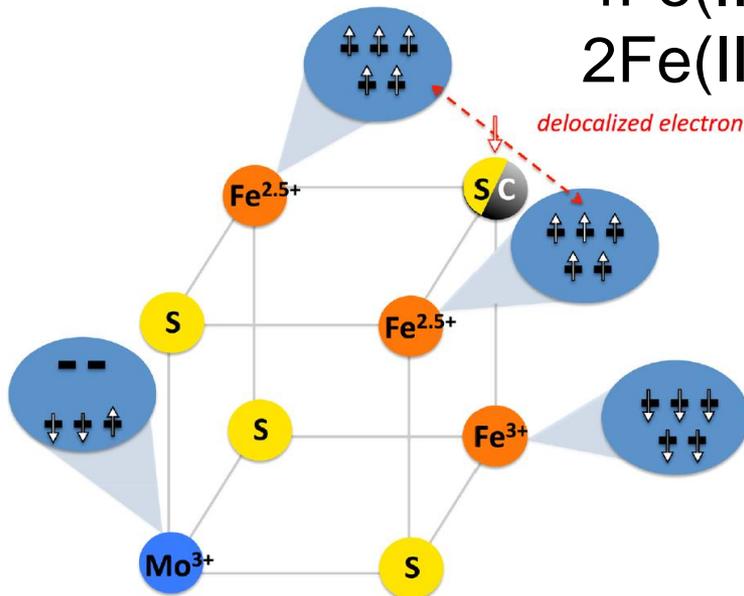
# Struttura elettronica di FeMo-co

Resting state:  $S = 3/2$

- |   |                       |                       |
|---|-----------------------|-----------------------|
| 1) $[\text{MoFe}_7\text{S}_9\text{C}]^{3-}$ | 6Fe(II)1Fe(III)Mo(IV) |                       |
| 2) $[\text{MoFe}_7\text{S}_9\text{C}]^{1-}$ | 4Fe(II)3Fe(III)Mo(IV) | Mo(IV), $d^2$ $S = 0$ |
| 3) $[\text{MoFe}_7\text{S}_9\text{C}]^{1+}$ | 2Fe(II)5Fe(III)Mo(IV) |                       |

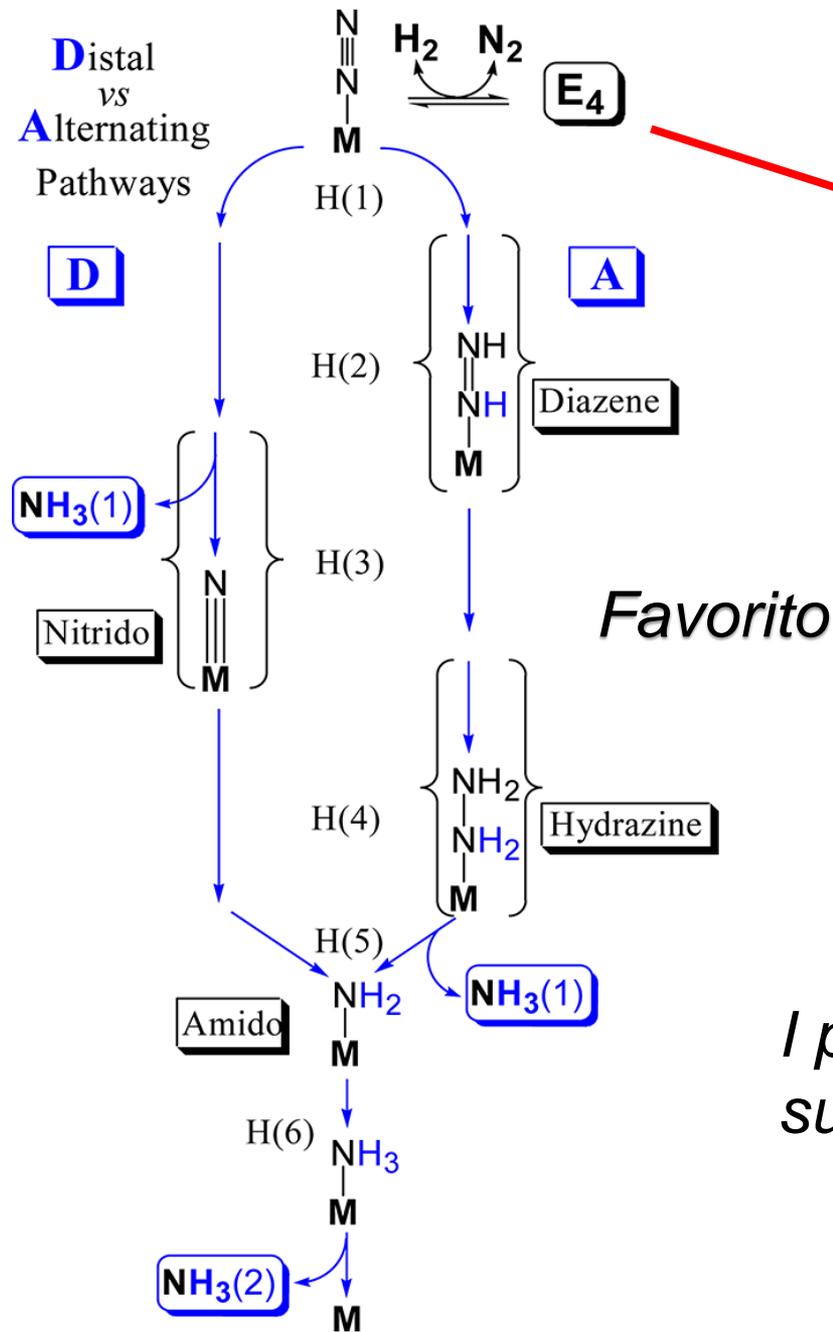
2014: Mo(III),  $d^3$  basso spin ( $\uparrow\uparrow\downarrow$ )? (violazione della regola di Hund)

- |                       |               |                        |
|-----------------------|---------------|------------------------|
| 6Fe(II)1Fe(III)Mo(IV) | $\rightarrow$ | 5Fe(II)2Fe(III)Mo(III) |
| 4Fe(II)3Fe(III)Mo(IV) | $\rightarrow$ | 3Fe(II)4Fe(III)Mo(III) |
| 2Fe(II)5Fe(III)Mo(IV) | $\rightarrow$ | 1Fe(II)6Fe(III)Mo(III) |

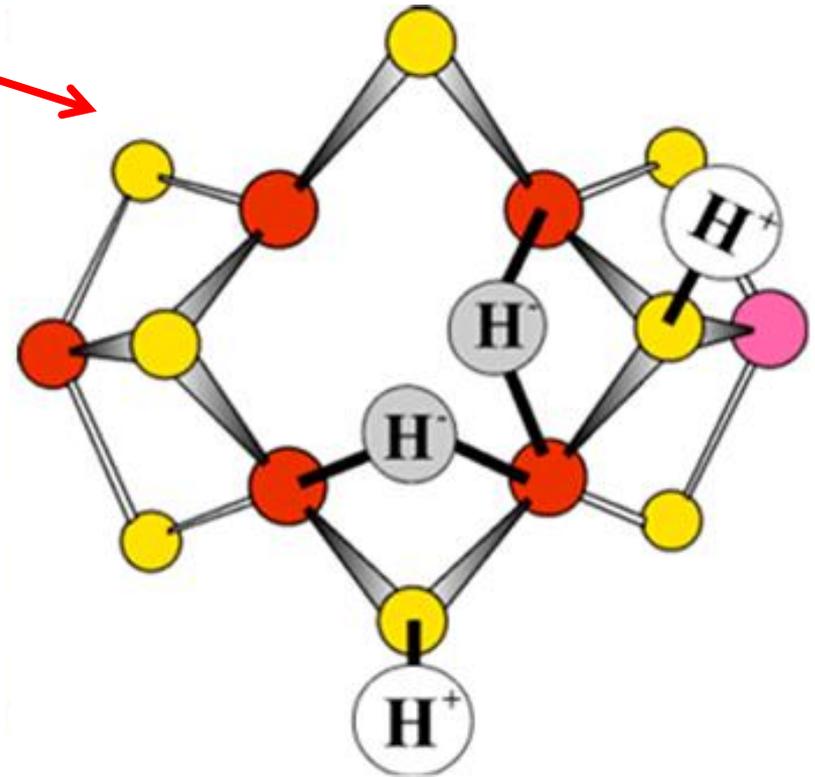


Cluster modello  $[\text{MoFe}_3\text{S}_3\text{C}]^{1+}$  e  $[\text{MoFe}_3\text{S}_4]^{3+}$

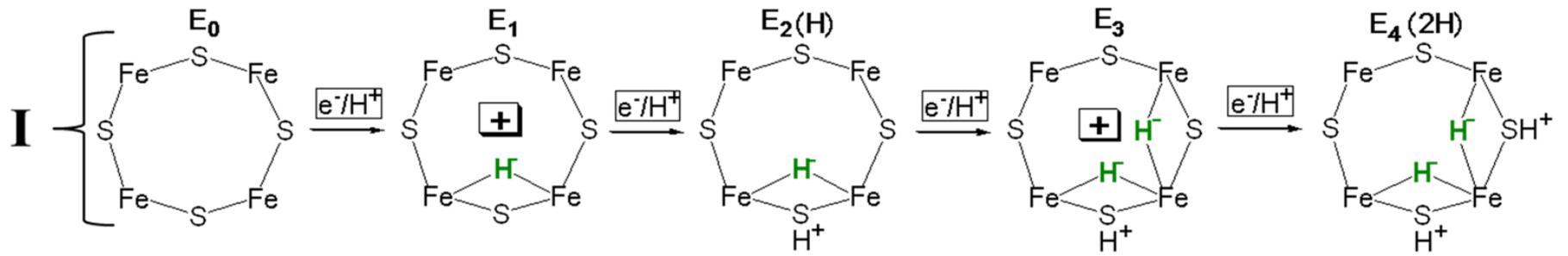




## Modello di E<sub>4</sub>

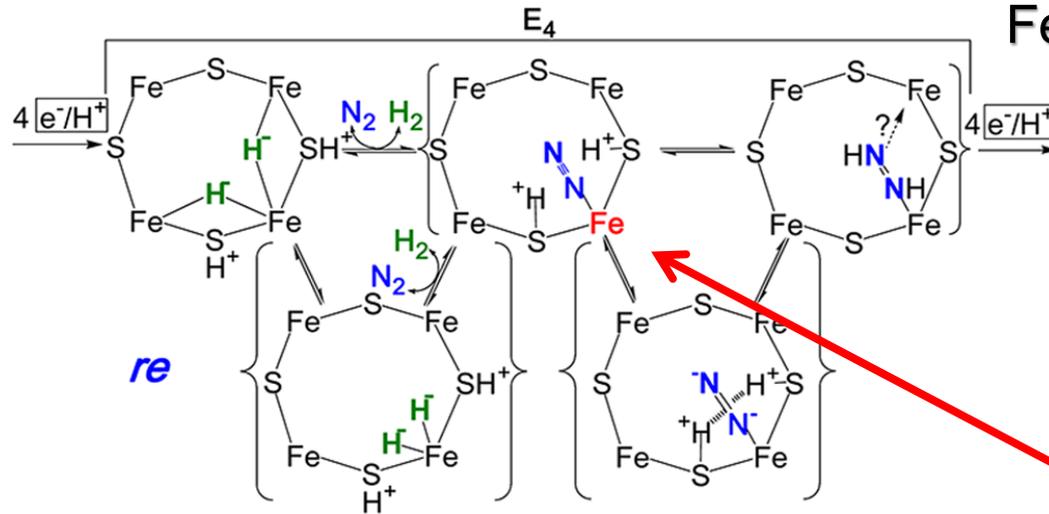


*I primi 4 elettroni si accumulano sugli idruri e non sugli atomi di ferro*

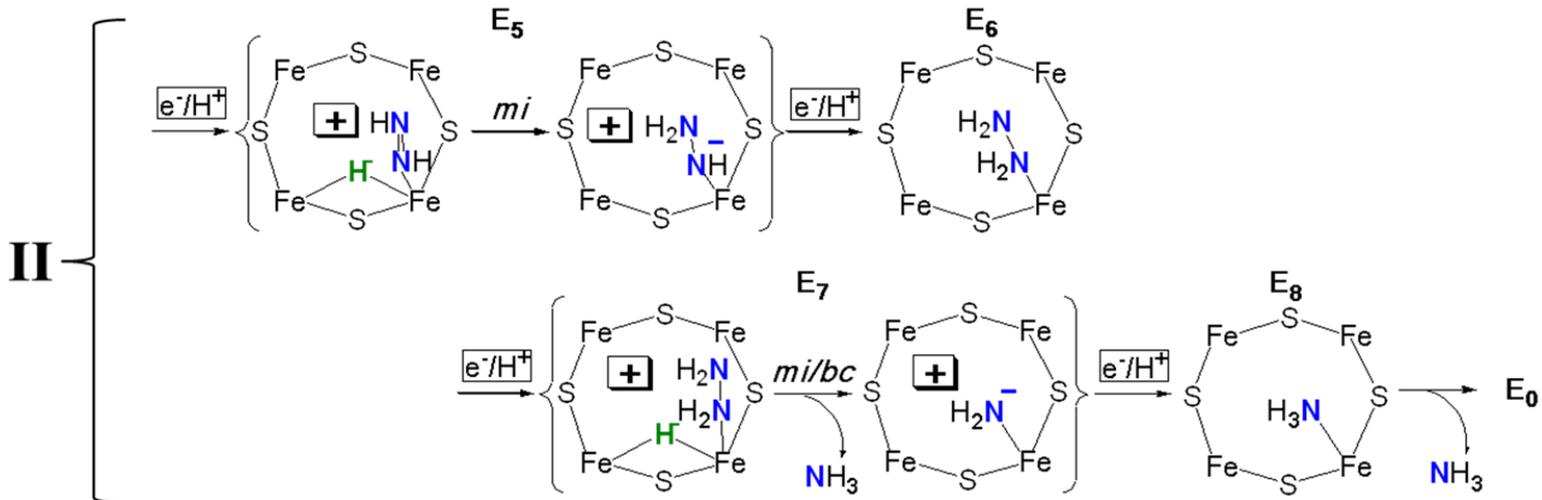


**FeMoco attivato**

Nel ciclo catalitico il FeMoco cambia di una sola unità il suo stato di ossidazione complessivo ( $E_n$  dispari)

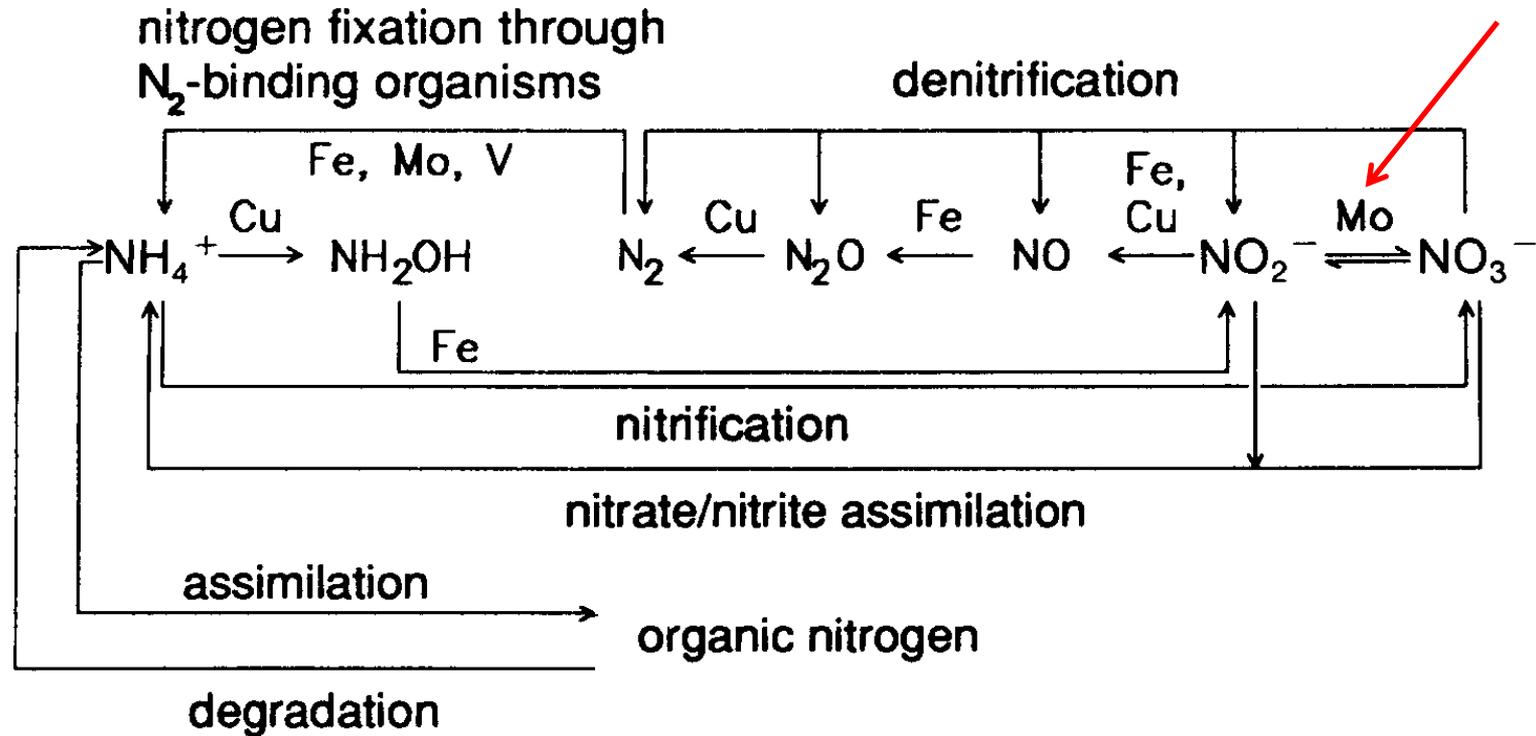


**Fe(0)?**



# Altri enzimi al molibdeno

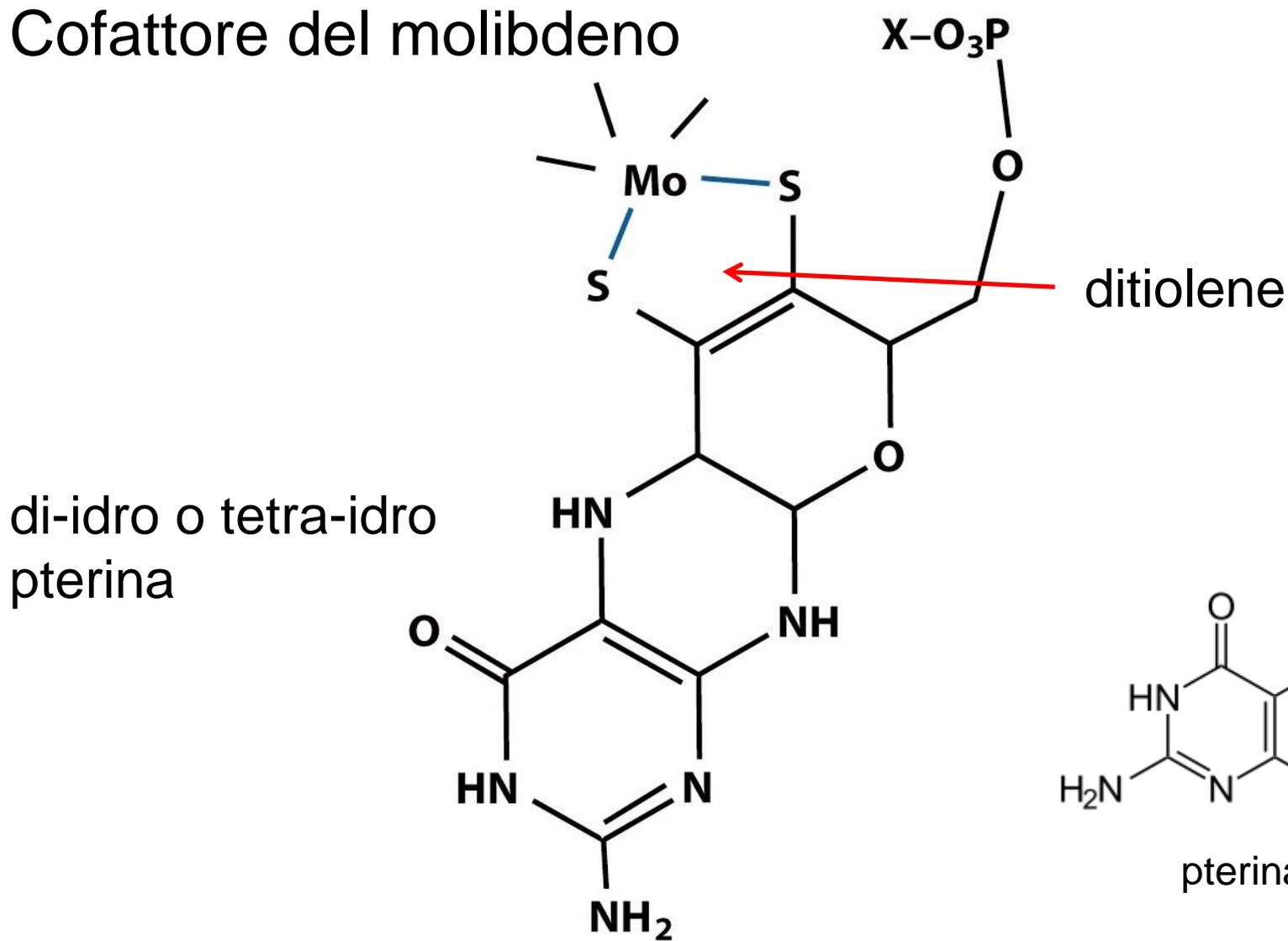
*catalizzano la ossidazione o la riduzione di piccole molecole*



Tre famiglie di enzimi al Mo (*osso-trasferasi*)

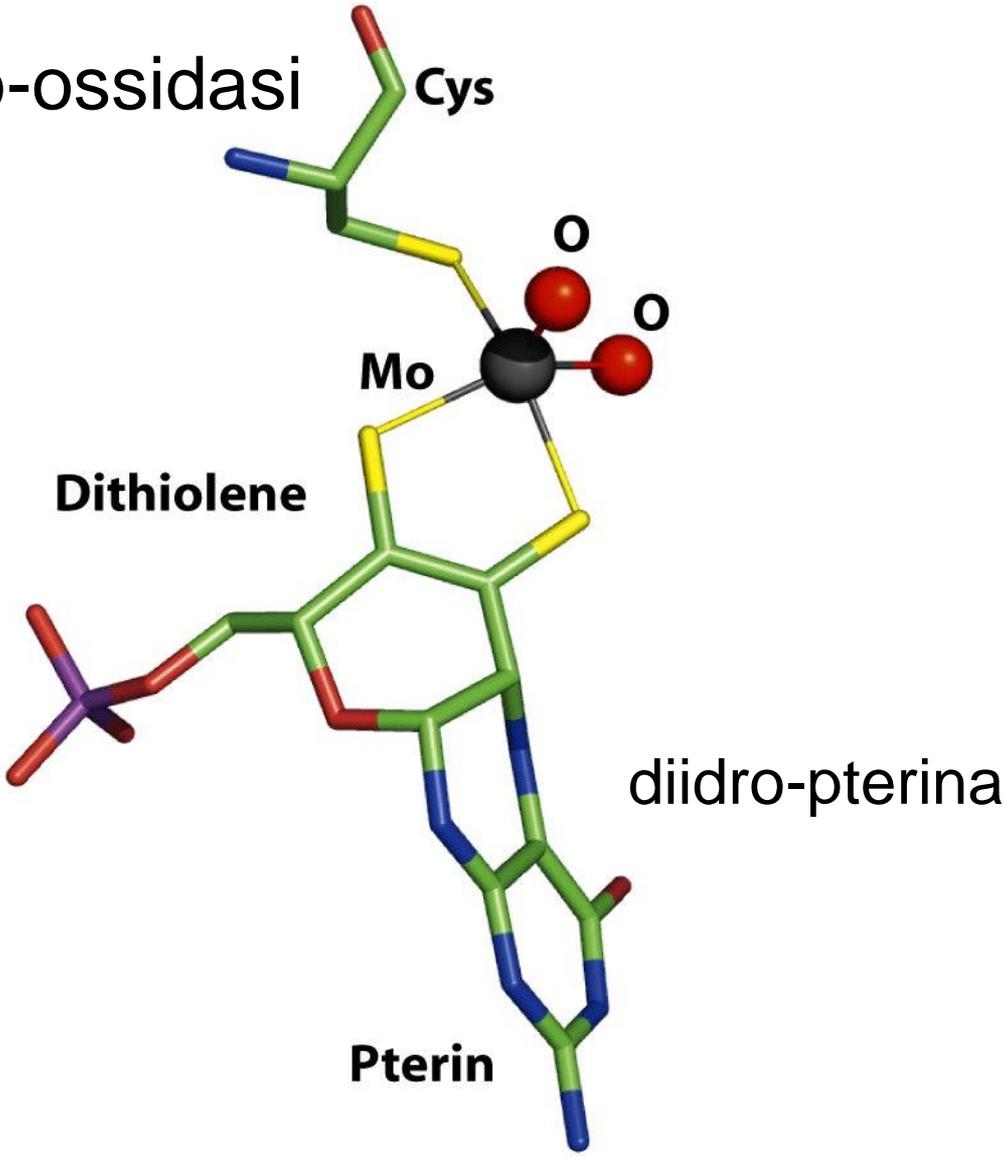
- xantina-ossidasi
- solfito-ossidasi
- DMSO-riduttasi

# Cofattore del molibdeno

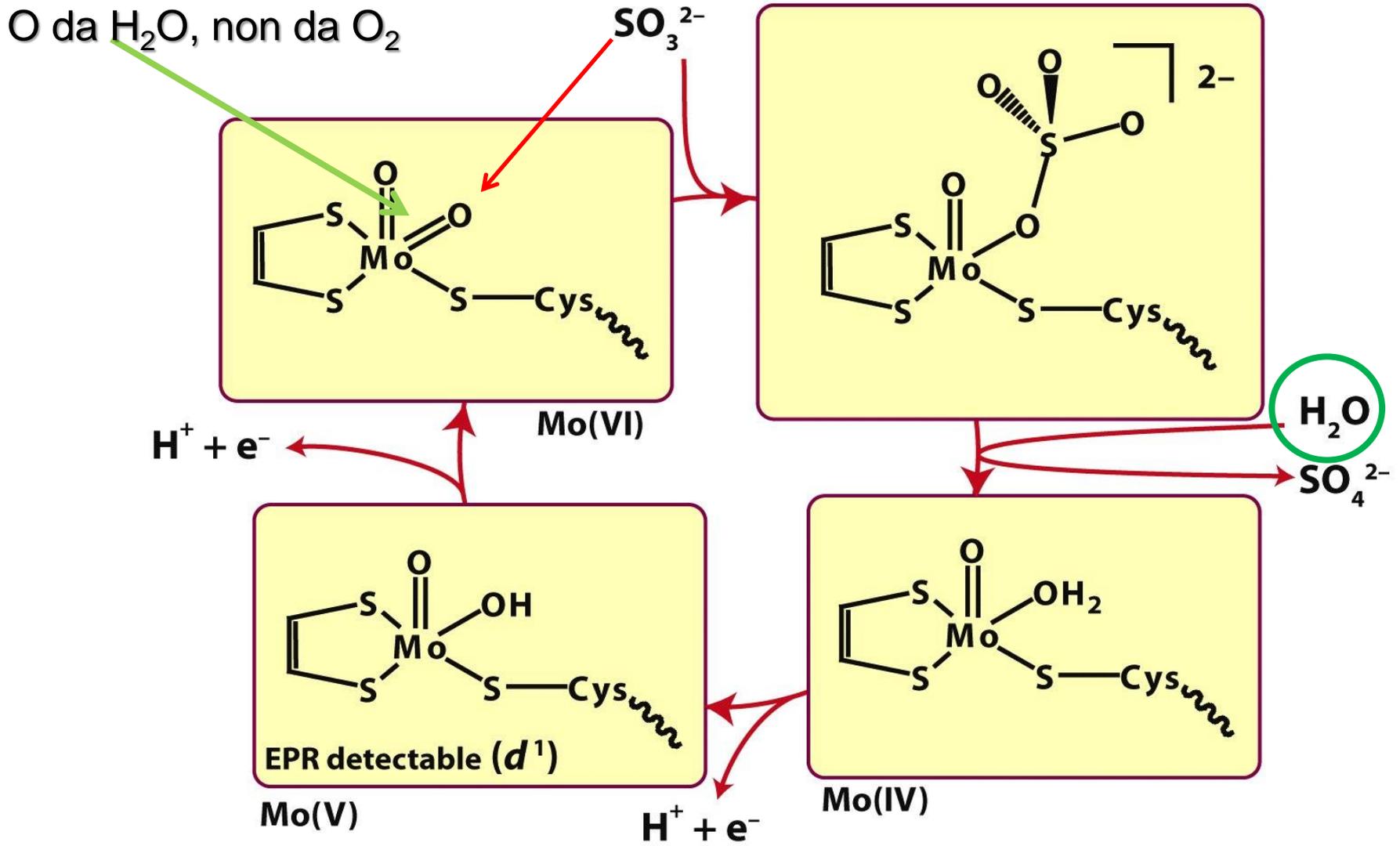


**Molybdopterin as ligand**

# Sito della solfito-ossidasi

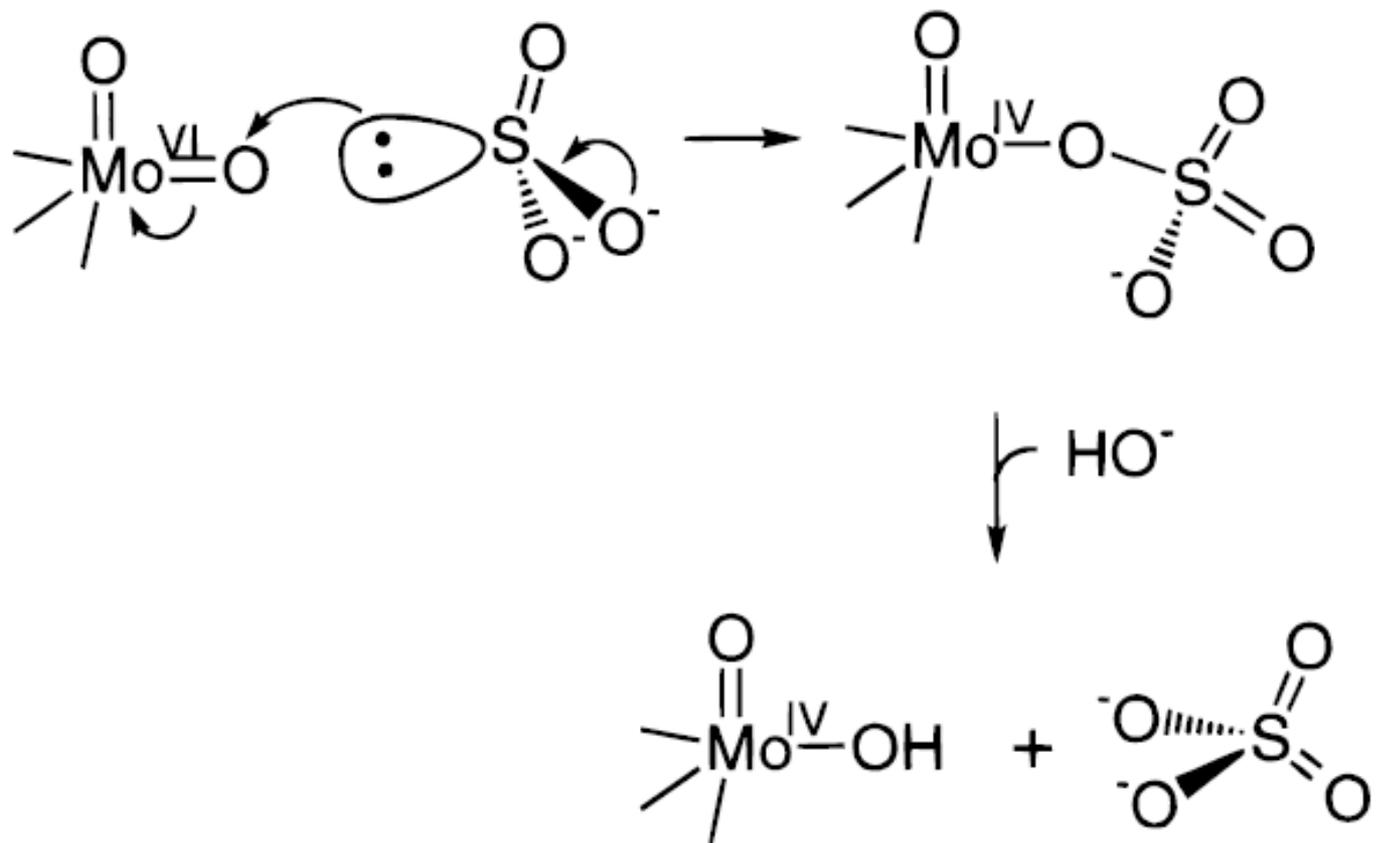


# Ciclo catalitico della solfito-ossidasi

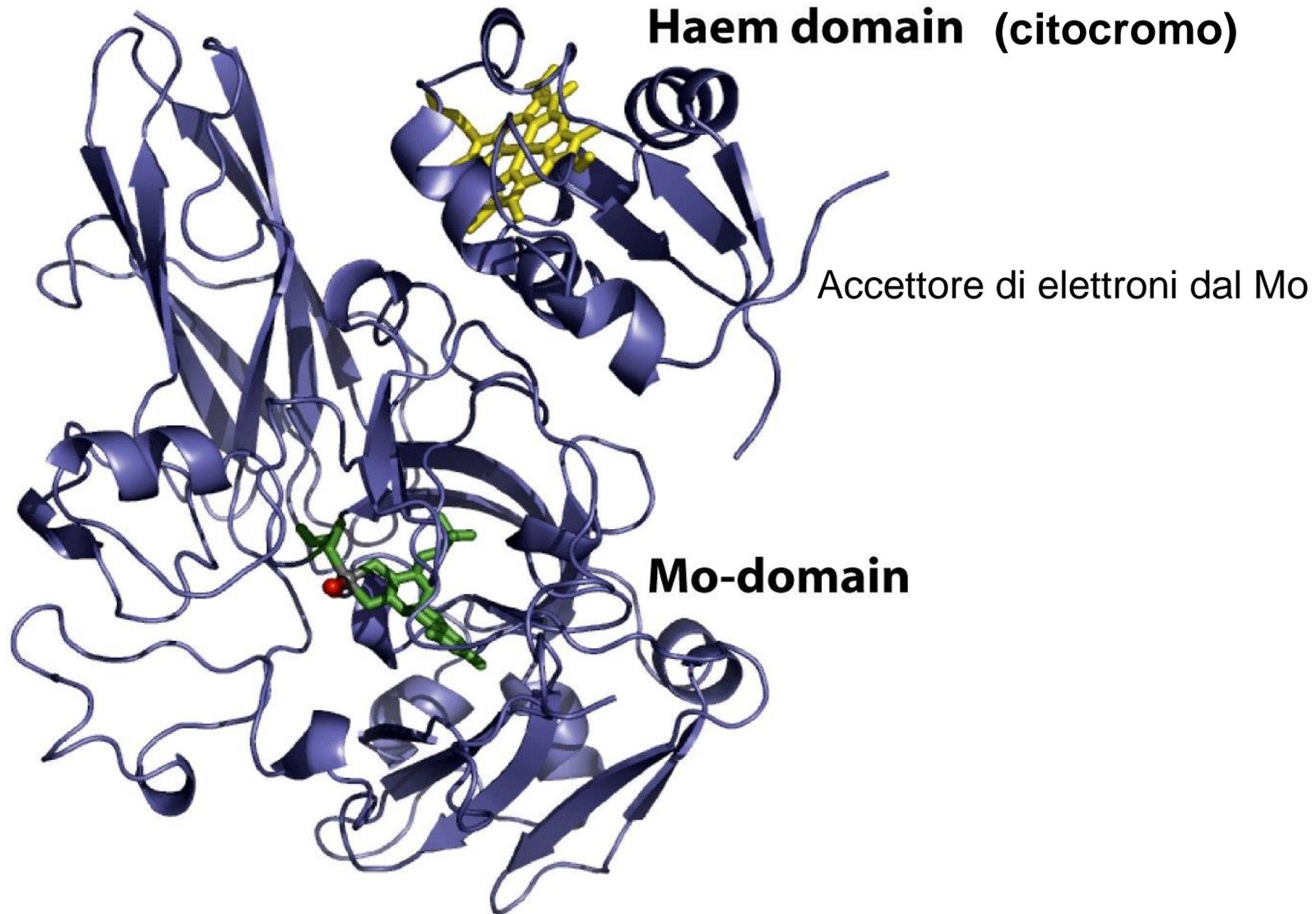


Mo possiede tre stati di ossidazione stabili, Mo(IV), Mo(V) e Mo(VI)

# Dettaglio del meccanismo di trasferimento di ossigeno



# Struttura della solfito-ossidasi



# Scala di entalpia delle reazioni di trasferimento di atomi di ossigeno

