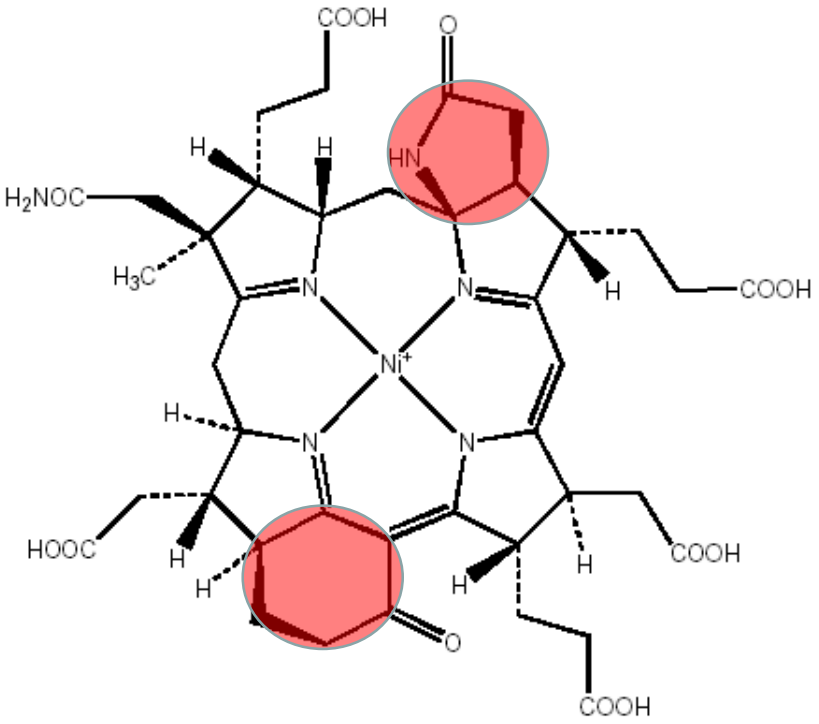
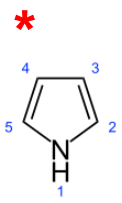
Nickel in Biological Chemistry

Coenzyme F430: involved in the conversion of CO_2 to CH_4

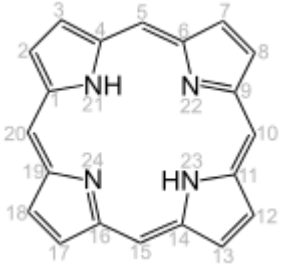


Coenzyme F430

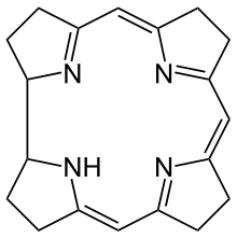
This is a tetrapyrrole* macrocycle but unlike other tetrapyrroles we have already encountered like the heme group, the macrocycle is more highly saturated and hence is less rigid.



pyrrole



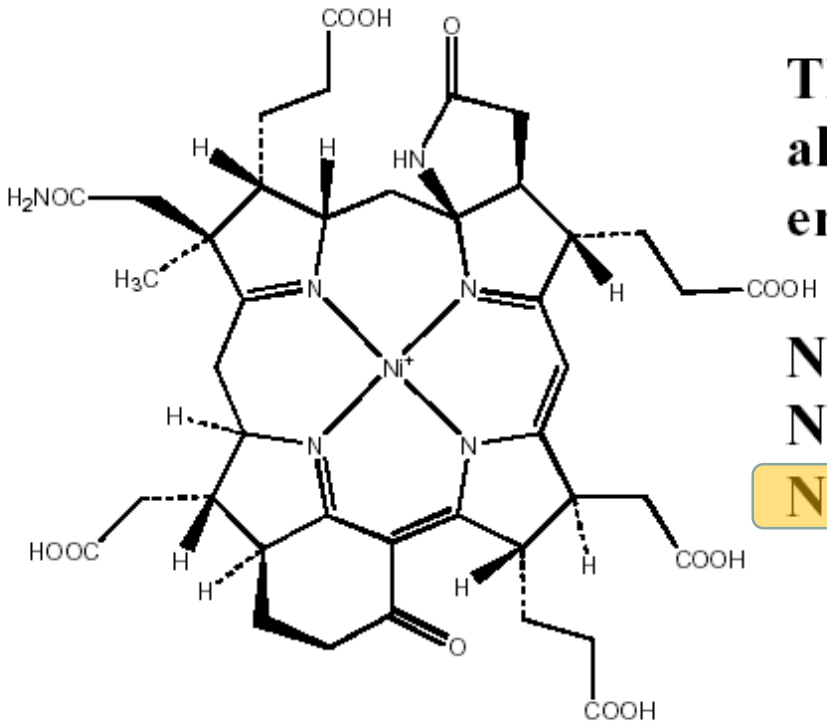
Porphirin → Tetrapyrrole → heme



corrin → cobalamin

Nickel in Biological Chemistry

Coenzyme F430



The flexibility of the macrocycle allows the nickel coordination environment to change.

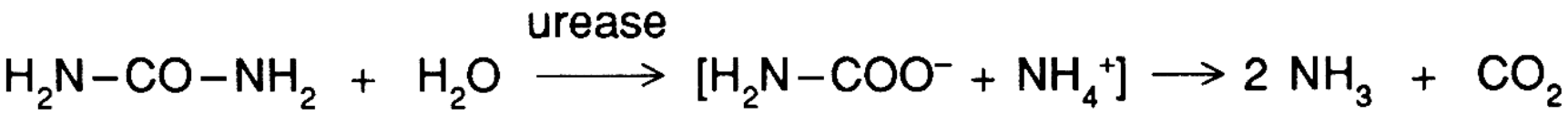
Ni(II)-N (high spin)	2.10 A
Ni(II)-N (low spin)	1.90 A
Ni(I)-N	2.00 A

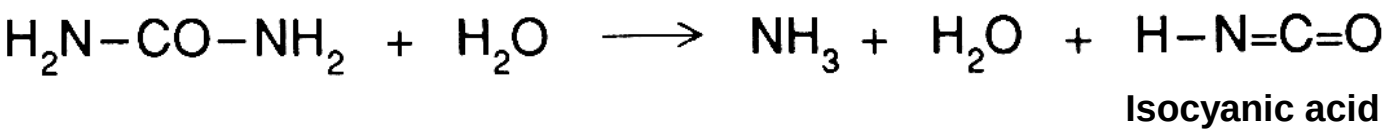
This may allow the nickel to change spin state or oxidation state easily* allowing it to function as a coordination site for methyl groups. This co-factor is involved in the conversion of carbon dioxide to methane.

* Already seen in the blue copper proteins

Nickel in Biological Chemistry

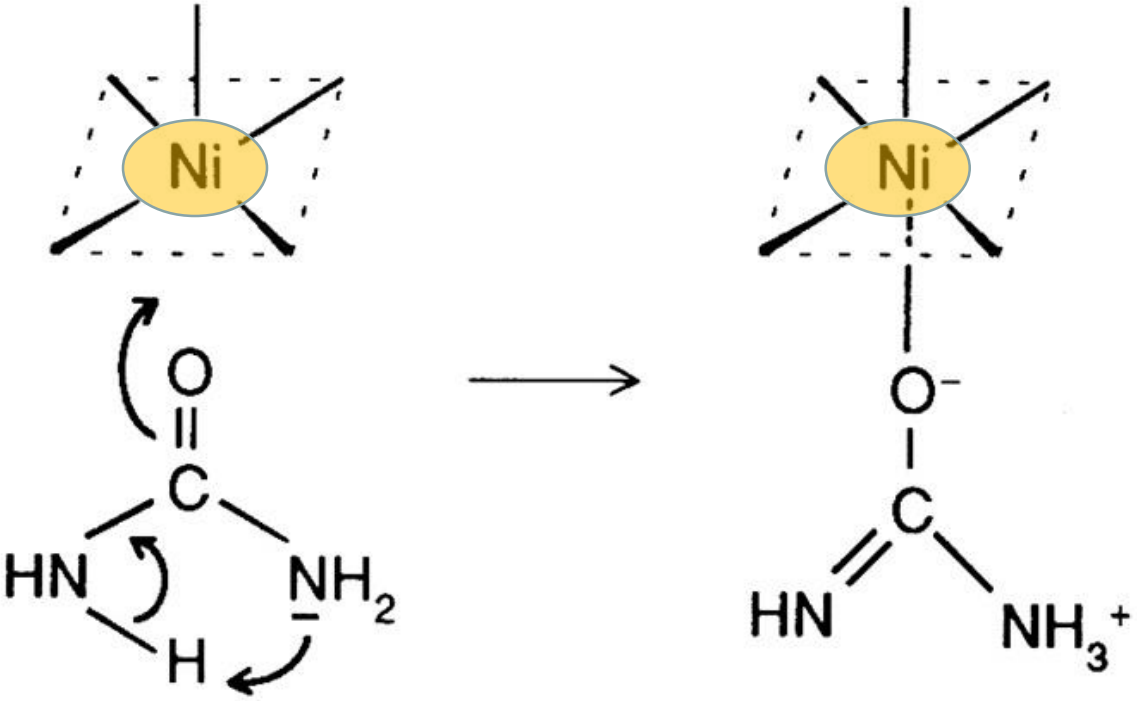
Urease





- **Urea is a very stable molecule and its spontaneous hydrolysis is very very slow!**
- **The half-life value of the uncatalyzed reaction is 3.6 YEARS at 38°C!!!**
- **The catalytic activity of the enzyme increases the rate of hydrolysis by a factor of about 10^{14}.**

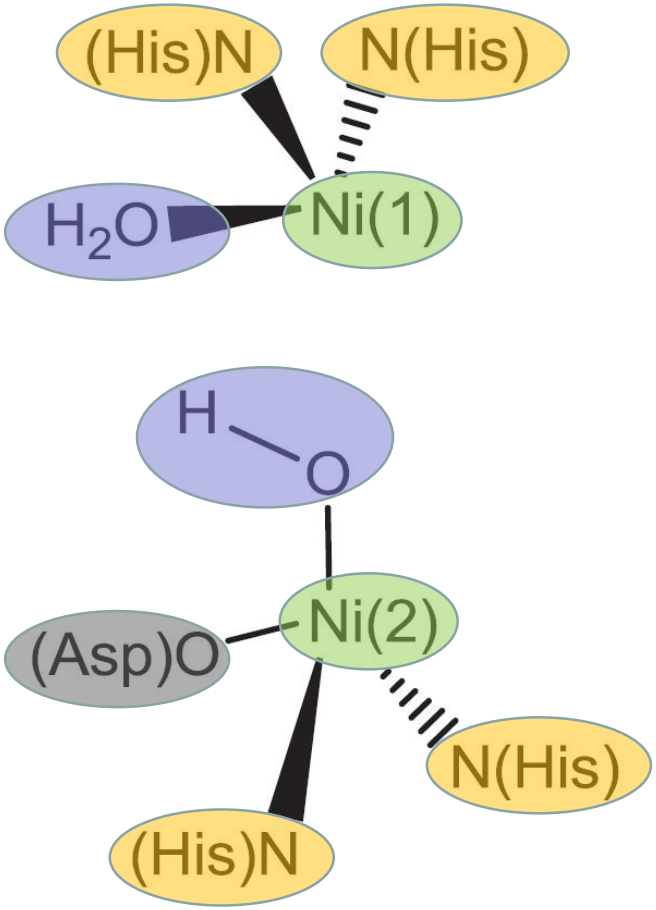
A metal substrate binding seems to be play a key role in the catalyzed process



Support for the metal substrate binding comes from the fact that phosphate derivatives binding strongly to Nickel, inhibit the activity of the enzyme

Little structural information available regarding the nickel centers in the active site

The enzyme consists of 6 equivalent subunits. Each subunit contains 2 close but apparently different nickel ions



Electrophilic attack of one of the nickel centers on the carbonyl oxygen

nucleophilic attack of a nickel hydroxo species on the carbonyl center

push–pull mechanism