Magnetic Properties of Coordination Complexes

Diamagnetic Compounds: Those, which tend to move out of a magnetic field.
Example: N_2

Paramagnetic Compounds: Those, which tend to move into a magnetic field.
Example: O_2

The extent of paramagnetism is measured in terms of the **magnetic moment, μ**. The larger the magnitude of μ, greater the paramagnetism of the compound.

Magnetic moment has contributions from spin and orbital angular momentum. A non-spherical environment may lead to quenching of the contribution from orbital angular momentum.

However, the spin-only magnetic moment survives in all cases and is related to the total number of unpaired electrons.

$$\mu_{eff} = \mu_{s.o} = 2\sqrt{S(S+1)} = \sqrt{n(n+2)}\ \text{BM}$$

Magnetic Properties of Coordination Complexes

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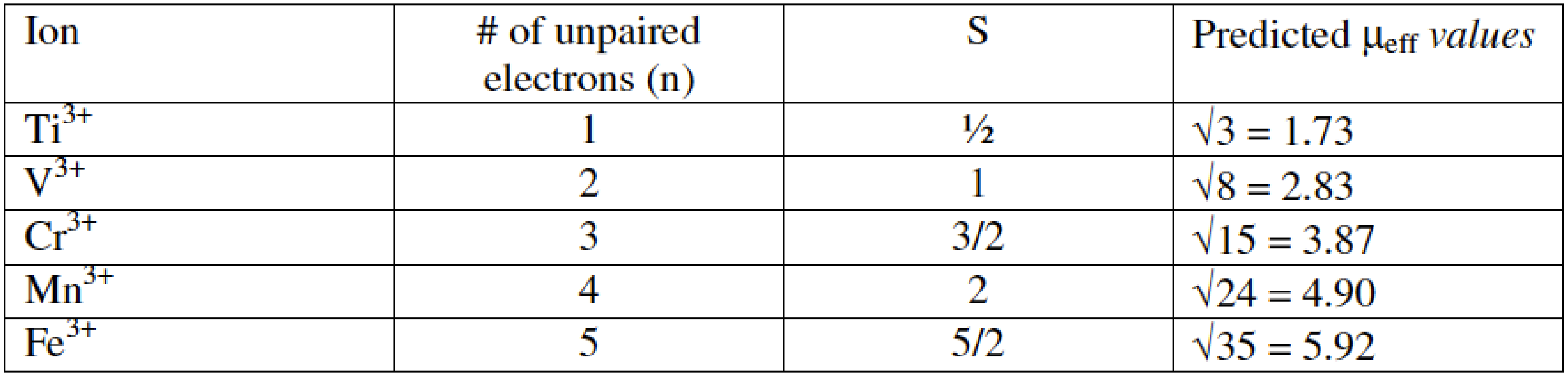


Ion	# of unpaired electrons (n)	S	Predicted μ_{eff} *values*
Ti^{3+}	1	½	$\sqrt{3} = 1.73$
V^{3+}	2	1	$\sqrt{8} = 2.83$
Cr^{3+}	3	3/2	$\sqrt{15} = 3.87$
Mn^{3+}	4	2	$\sqrt{24} = 4.90$
Fe^{3+}	5	5/2	$\sqrt{35} = 5.92$

If there is a possibility for contribution from the orbital angular momentum,

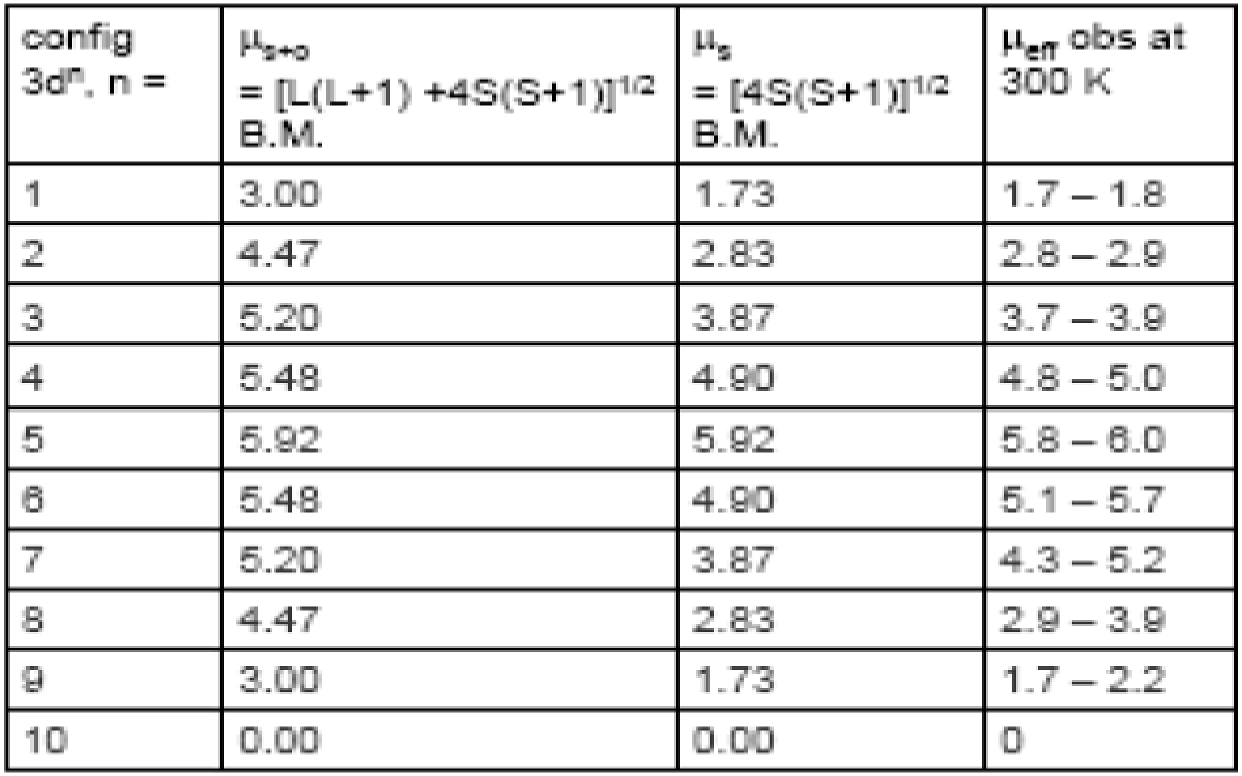
$$\mu = \sqrt{L(L+1) + 4S(S+1)}$$

For a given value of the orbital quantum number *l*, the magnetic quantum number *m* can have any values from –*l* to +*l* and L = sum of *m*

For *d* orbital electrons, *m* = 2, 1, 0, -1, -2

If there is only one electron in the *d* orbitals, L = 2

Magnetic Properties of Coordination Complexes

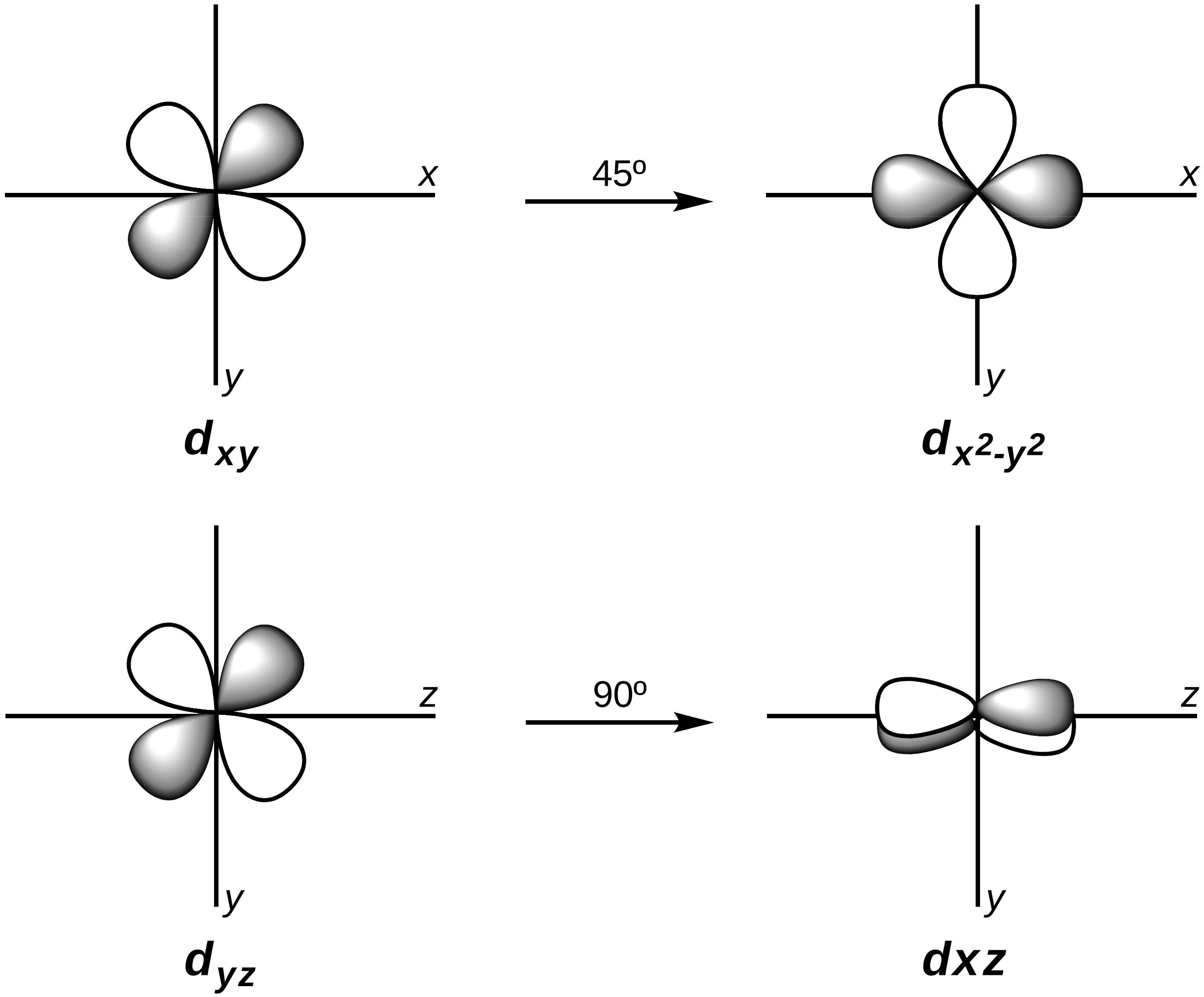


config $3d^n$, n =	μ_{s+o} = $[L(L+1) + 4S(S+1)]^{1/2}$ B.M.	μ_s = $[4S(S+1)]^{1/2}$ B.M.	μ_{eff} obs at 300 K
1	3.00	1.73	1.7 – 1.8
2	4.47	2.83	2.8 – 2.9
3	5.20	3.87	3.7 – 3.9
4	5.48	4.90	4.8 – 5.0
5	5.92	5.92	5.8 – 6.0
6	5.48	4.90	5.1 – 5.7
7	5.20	3.87	4.3 – 5.2
8	4.47	2.83	2.9 – 3.9
9	3.00	1.73	1.7 – 2.2
10	0.00	0.00	0

$K_3[Fe(CN)_6]$ has a magnetic moment of 2.3 B.M., which is a d^5 low-spin complex with one unpaired electron.

$[Fe(H_2O)_6]^{3+}$ ions are high-spin with 5 unpaired electrons. It has a magnetic moment of 6 B.M.

Magnetic Properties of Coordination Complexes



For an octahedral complex, orbital contributions are possible only when the t_{2g} orbitals are differentially occupied and for a tetrahedral complex the t_2 orbitals have to be differentially occupied.

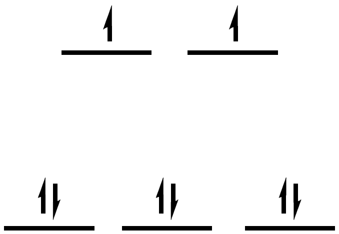
Magnetic Properties of Coordination Complexes

Consider a Ni(II) complex, electronic configuration is d^8

For a free metal ion,

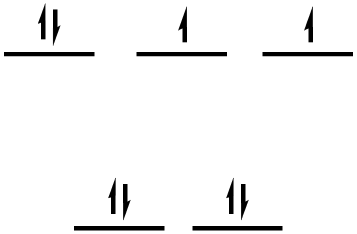
$S = 1$, $L = 3$ and $\mu = \sqrt{L(L+1) + 4S(S+1)} = 4.47$ B.M.

For an octahedral complex,



Orbital contribution is zero and magnetic moment is close to the spin only value

For a tetrahedral complex,



Magnetic moment is higher than the spin only value as there is positive orbital contribution

Magnetic Properties of Coordination Complexes

Co(II) d^7

K_2CoCl_4

Blue

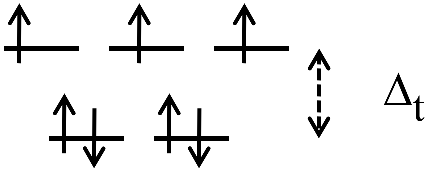
moisture

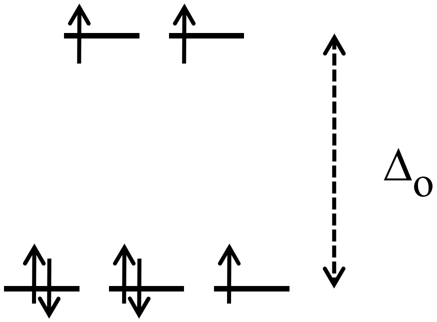
⟷

heat

$[Co(H_2O)_6]Cl_2$

Pink

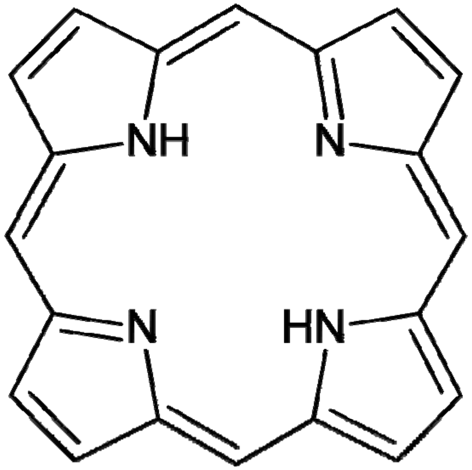




No orbital contribution
Magnetic moment $\mu = 3.73$ BM

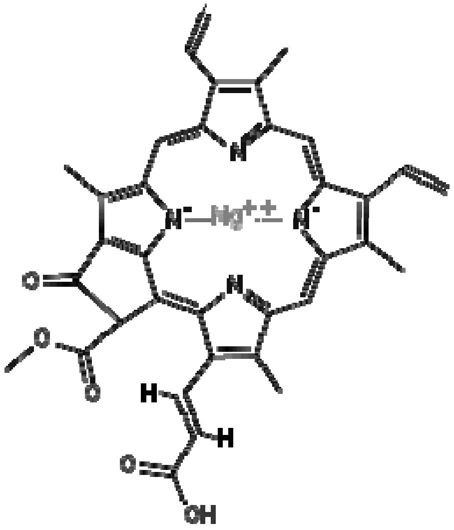
Orbital contribution
Magnetic moment $\mu = 4.2$ B.M.
higher than spin-only value

Coordination Complexes in Biological Systems

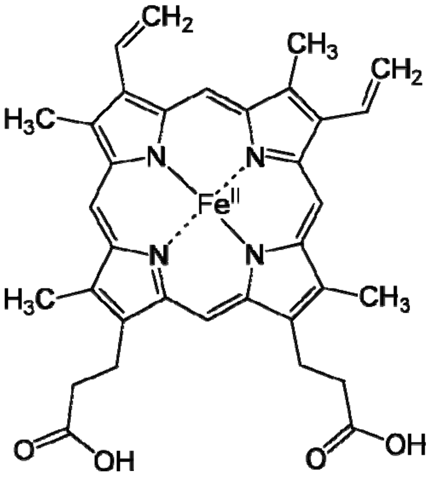


Porphine

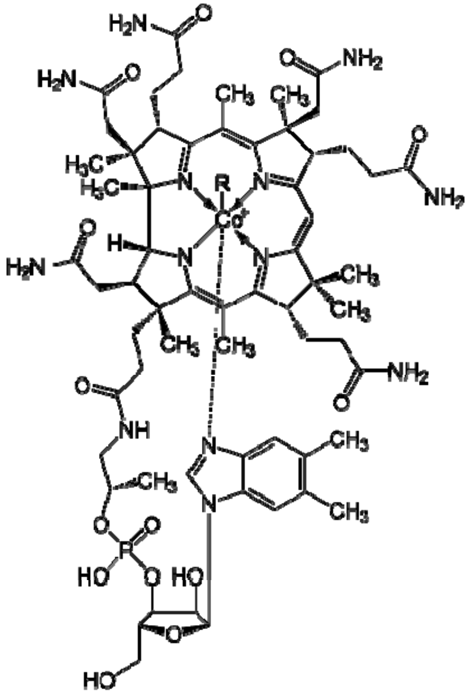
Porphyrins are heterocyclic macrocycles composed of four modified interconnected pyrrole subunits. They form coordination complexes with metal ions and are found in biological systems.



Chlorophyll *c2*



Heme B



Cobalamin

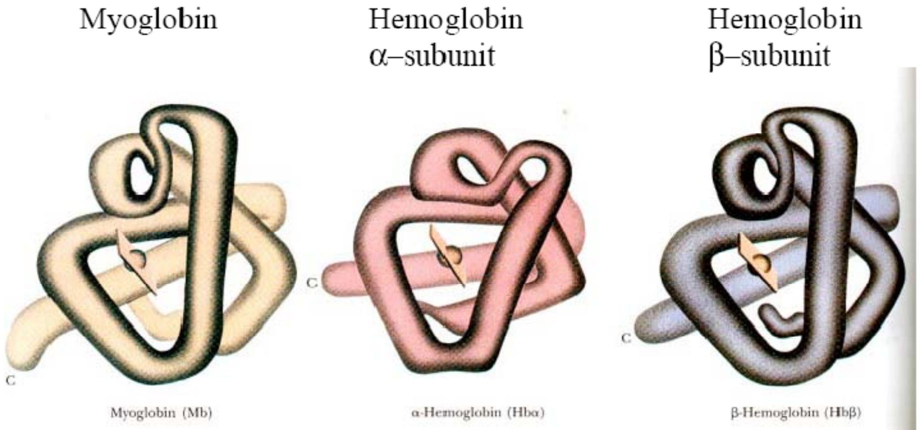
Hemoglobin and Myoglobin

Hemoglobin (Hb)

- MW= 64,500 g
- $\alpha_2\beta_2$
- α= 141 residues
- β= 146 residues
- active site: Fe(por)
- function: cooperatively binds and transports O_2

Myoglobin (Mb)

- MW= 17,800 g
- α
- α= 161 residues
- active site: Fe(por)
- function: binds and transports O_2

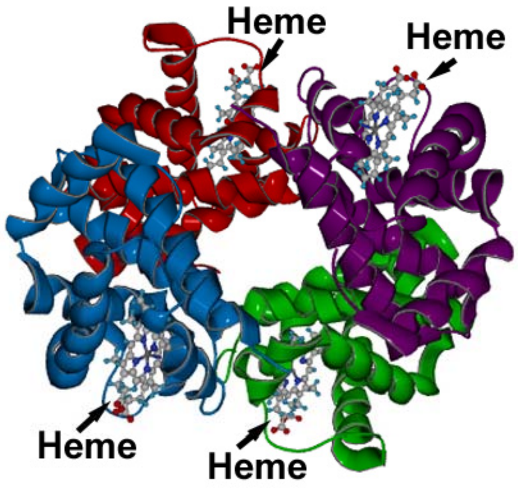


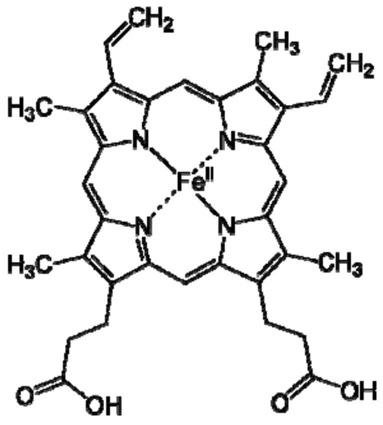
Myoglobin (Mb) α-Hemoglobin (Hbα) β-Hemoglobin (Hbβ)

Figure **12.14** Conformational drawings of the α- and β-chains of Hb and the myoglobin chain.

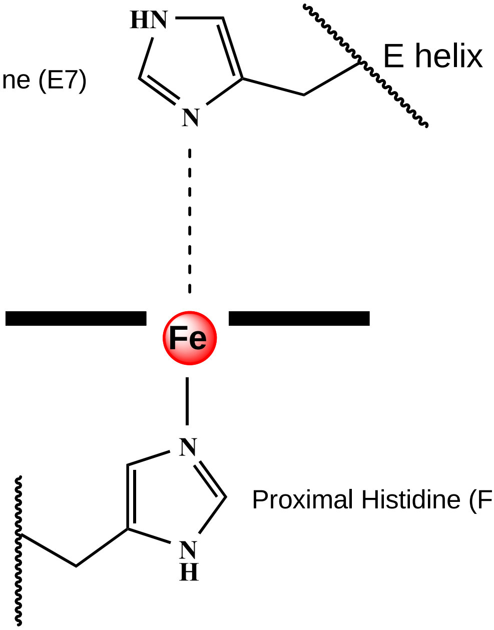
Notice that the hemoglobin is essentially a tetramer of myoglobin. (There are four myoglobin like units in hemoglobin.)

Oxygenated and Deoxygenated Forms

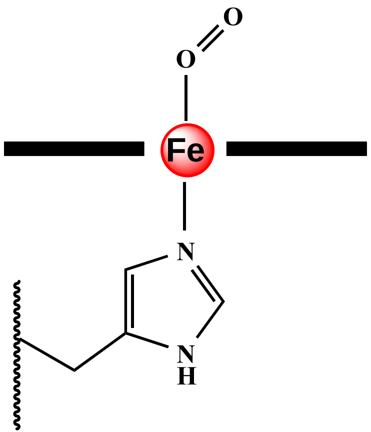




Distal Histidine (E7)

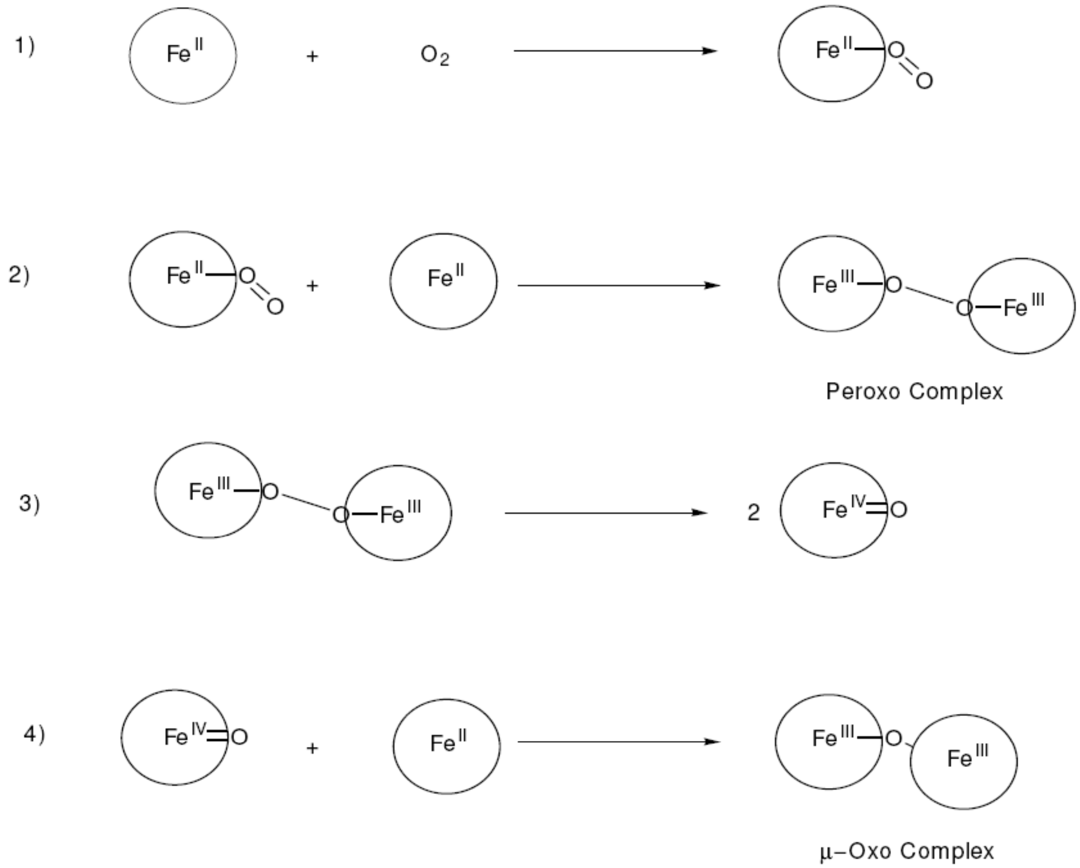


Proximal Histidine (F8)

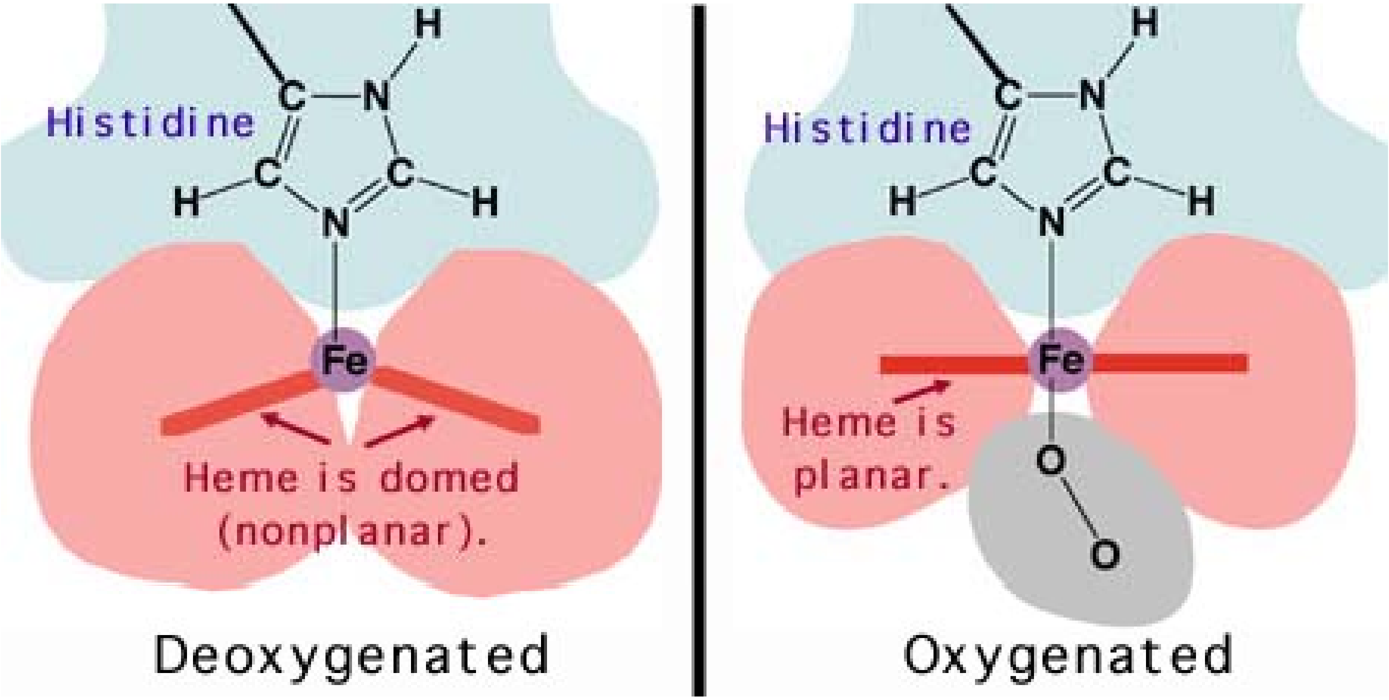


Proximal Histidine (F8)

The Role of the Protein



Hemoglobin and Myoglobin

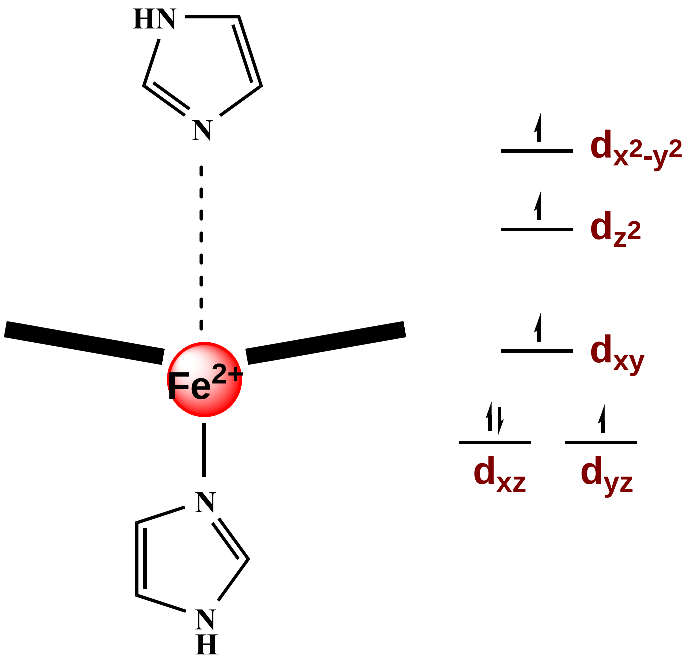


∠Fe-O-O = 150º

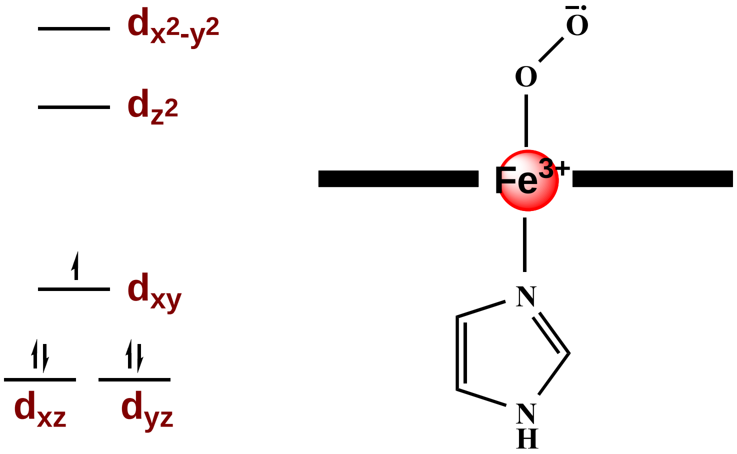
Raman Spectra gives $\nu_{o\text{-}o}$ at 1105 cm^{-1}.indicating that the complex should be in a superoxide state

	O_2	O_2^-	O_2^{2-}
$\nu_{o\text{-}o}$ (cm^{-1})	1560	1100	850-740

Coordination Environment of Fe



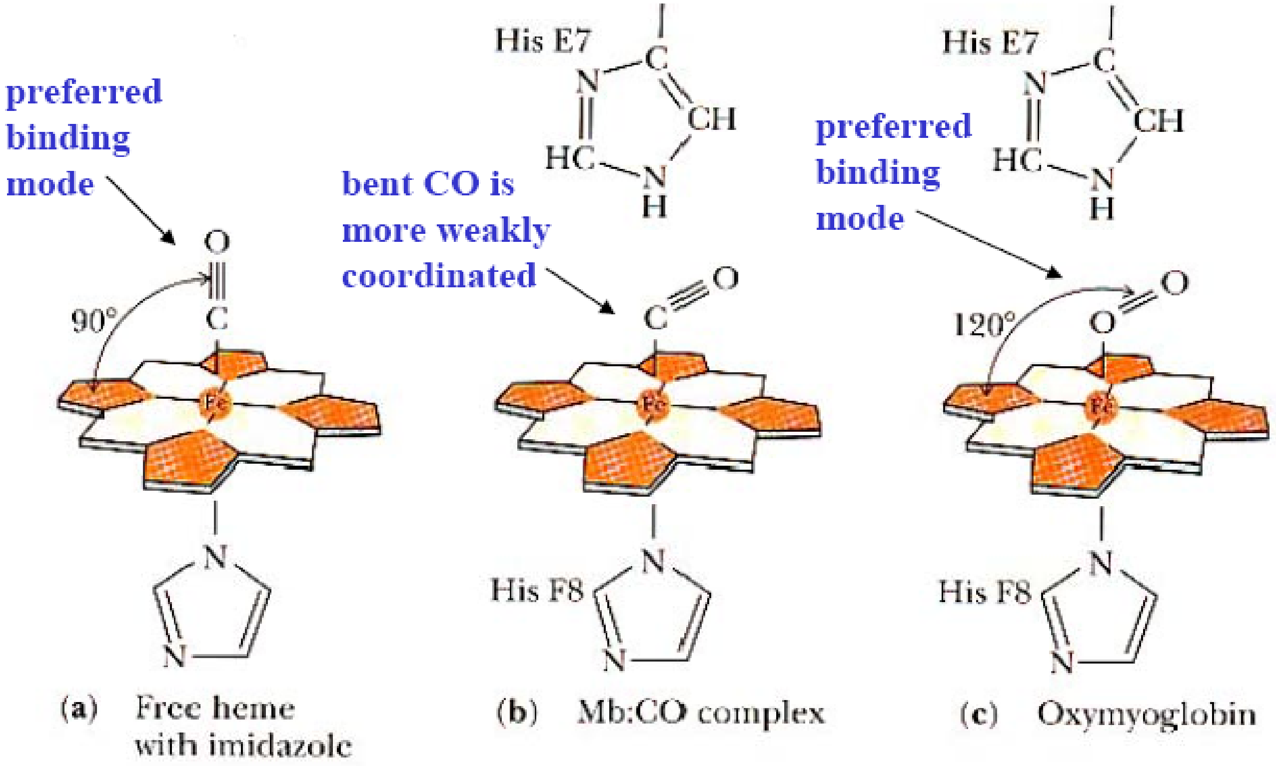
Total unpaired electrons = 4, S = 2
Deoxygenated form is high-spin and paramagnetic



Total unpaired electrons = 1, S = 1/2
Oxygenated form is low-spin
The magnetic moment of Fe^{3+} and the superoxide radical involves in anti-ferromagnetic coupling and the oxygenated complex is not paramagnetic

Hemoglobin and Myoglobin

Role of the distal base



preferred binding mode

bent CO is more weakly coordinated

preferred binding mode

(a) Free heme with imidazole

(b) Mb:CO complex

(c) Oxymyoglobin

Hemoglobin and Myoglobin

Cooperative Binding Curve for Hb