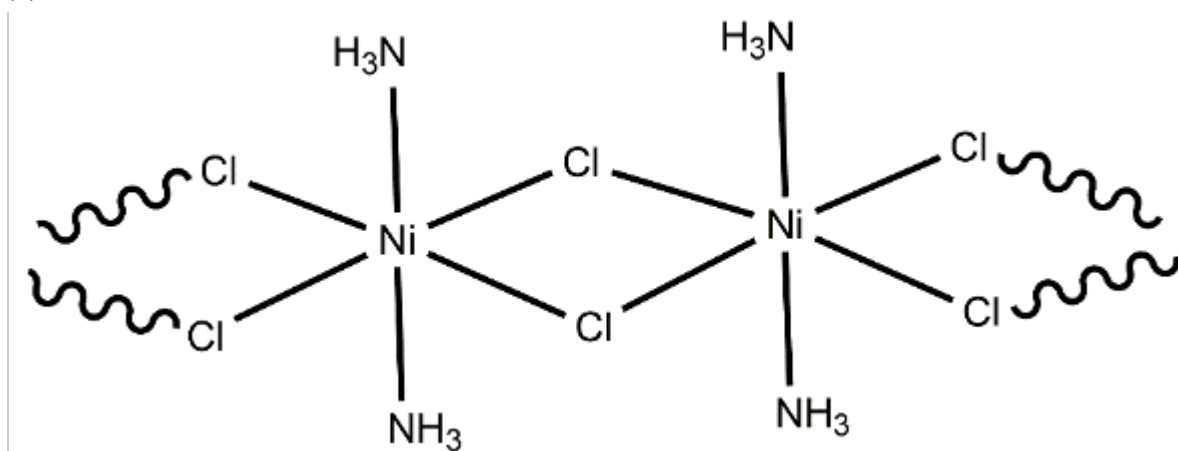


1. The following complexes have the indicated effective magnetic moments. Describe the structure and bonding of the complexes on the basis of the  $\mu_{\text{eff}}$  values (in B.M.).

- (a)  $\text{K}_2\text{NiF}_6$  ( $\mu_{\text{eff}} = 0$  B.M.)
- (b)  $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$  ( $\mu_{\text{eff}} = 3.3$  B.M.)
- (c)  $\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$  ( $\mu_{\text{eff}} = 0.0$  B.M.)
- (d)  $\text{Ni}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$  ( $\mu_{\text{eff}} = 3.95$  B.M.)

Ans. (a) Ni(IV) (d6) system. Low spin octahedral complex.

(b)



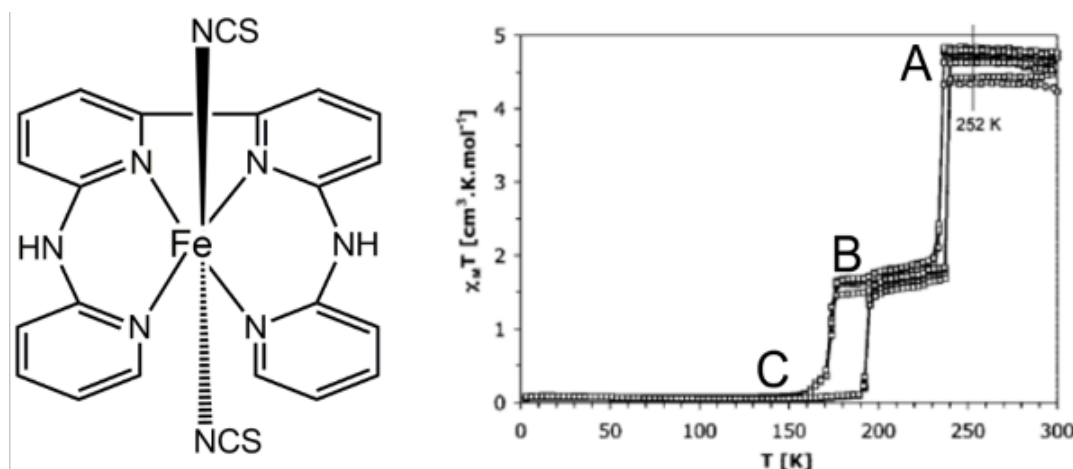
Bridged complex. Octahedral geometry.

Expected  $\mu_{\text{eff}} = 2.83$  B.M. It's a bit higher due to excited state contributions.

(c) Square planar d8 system.

(d) Steric hindrance. Leads to tetrahedral geometry. Expected  $\mu_{\text{eff}} = 2.83$  B.M. Orbital magnetic moment enhances the overall magnetic moment.

2. For the following octahedral iron complex, the effective magnetic moment (magnetic susceptibility) changes at 300 K (A,  $\mu_{\text{eff}} = 6.18 \text{ BM}$ ,  $c_M T = 4.8 \text{ cm}^3 \text{ K mol}^{-1}$ ), 240 K (B,  $\mu_{\text{eff}} = 3.45 \text{ BM}$ ,  $c_M T = 1.5 \text{ cm}^3 \text{ K mol}^{-1}$ ) and 150 K (C,  $\mu_{\text{eff}} = 0 \text{ BM}$ ,  $c_M T = 0 \text{ cm}^3 \text{ K mol}^{-1}$ ). Write the electronic configuration of the iron ion in the complex at step A and step C?



Ans. Based on the structure, it is understood that iron is in +2 oxidation state. At A,  $\mu_{\text{eff}} = 6.18 \text{ BM}$  for 4 unpaired electrons suggests that  $\text{Fe}^{2+}$  is in a high spin state ( $t_{2g}^4 e_g^2$ ).

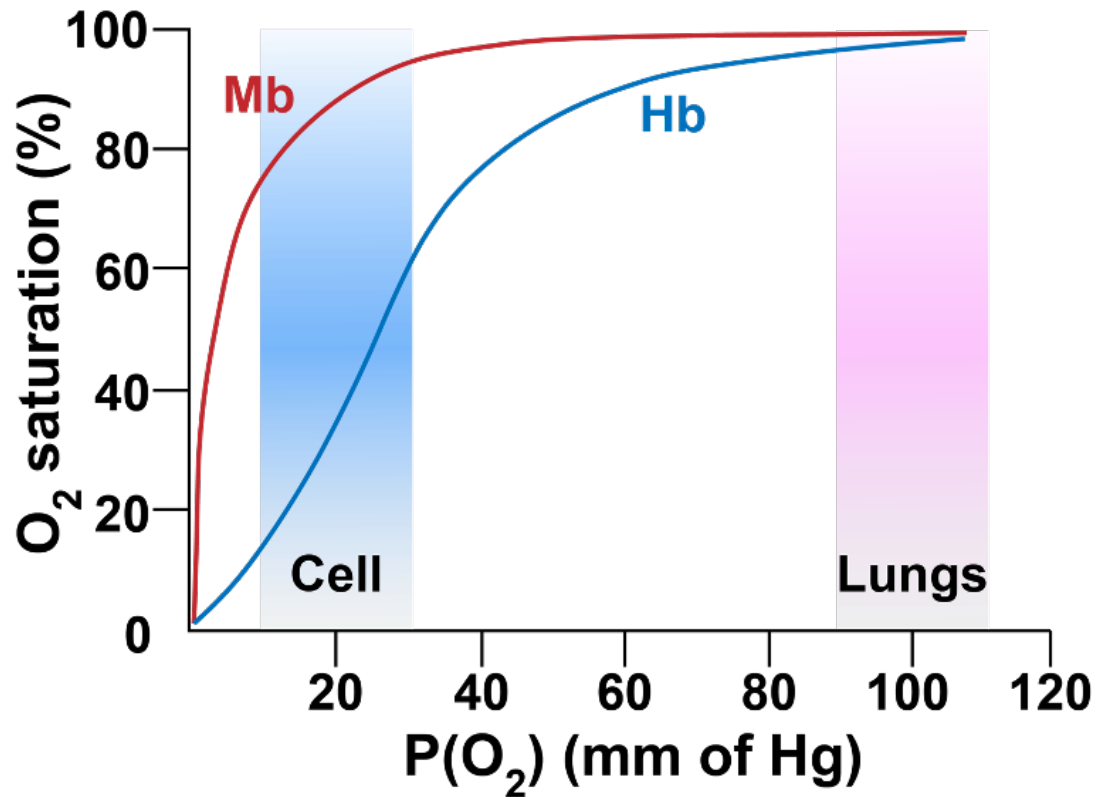
At C, due to a spin crossover from high spin to low spin, the magnetic moment becomes zero. Hence the configuration is ( $t_{2g}^6 e_g^0$ ).

3. For spin crossover systems, in the liquid state it is common to observe a gradual transition from low spin to high spin as a function of temperature. In the solid state, however, there is often an abrupt change in spin state at a certain temperature. Explain this difference and rationalize.

Ans. In the solution phase, long range cooperative interactions of spins are largely canceled out. So as temperature increases, the spin populations follow a nice Boltzmann distribution. In the solid state, the transition is more abrupt, hence sharp changes.

4. Why is the  $O_2$ -binding curve sigmoidal for hemoglobin; however, it is hyperbolic for myoglobin?

Ans.



Cooperative effect in Hb. Interaction between different subunits via salt bridge interactions to showcase the sigmoidal behavior.

Whereas in Mb, one single unit. No cooperativity effect. So hyperbolic behavior.