

CH105 INORGANIC: TUTORIAL-3

Q-IV.1. Calculate the ground state Term symbols for the following ions.

a) Ni^{2+} b) Dy^{3+} c) Ti^{2+} d) C

Answer:

$\text{Ni}^{2+} = {}^3\text{F}_4$; $\text{Dy}^{3+} = {}^6\text{H}_{15/2}$; c) $\text{Ti}^{2+} = {}^3\text{F}_2$ d) C = ${}^3\text{P}_0$

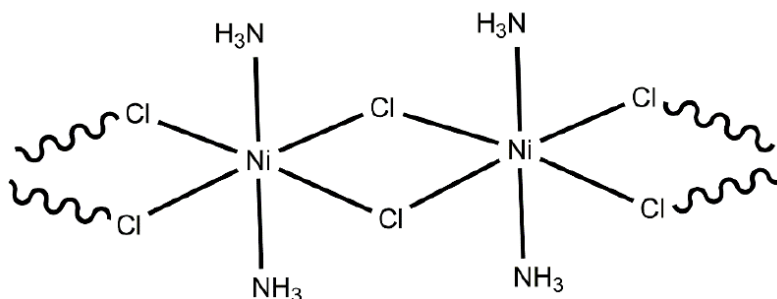
Q-IV.2. The following complexes have the indicated effective magnetic moments. Describe the structure and bonding of the complexes on the basis of the μ_{eff} values (in B.M.)

(a) K_2NiF_6 (0.0); (b) $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$ (3.3); (c) $\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$ (0.0); (d) $\text{Ni}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ (3.95)

(a) K_2NiF_6 (0.0); = Nickel is in +4 oxidation hence low spin $S = 0$.

(b) $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$ (3.3);

Ammonia is a strong field ligand hence tetrahedral geometry is not possible and square planar complex will give $S = 0$. This suggests that this complex likely to be octahedral and the geometry is



(c) $\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$ (0.0); Square planar and $S = 0$

(d) $\text{Ni}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ (3.95) = Tetrahedral and ground state orbital angular momentum hence large mag moment.

Q-IV.3. Identify the transition metal configurations both in the octahedral and tetrahedral environments which are expected to have an orbital contribution to the magnetic moment.

Octahedral (high spin)	Octahedral (low spin)	Tetrahedral
a) Fe^{3+} (No)	a) Fe^{3+} = (Yes)	a) Cr^{3+} = (Yes)
b) Fe^{2+} (Yes)	b) Fe^{2+} = (NA; $S = 0$)	b) Fe^{3+} = (No)
c) Ni^{2+} (No)	c) Co^{2+} = (No)	c) Mn^{3+} = (Yes)
d) Ti^{3+} (Yes)	d) Cr^{2+} = (Yes)	d) Fe^{2+} = (No)
e) Sc^{3+} (NA; $S = 0$)	e) Zn^{2+} = (NA; $S = 0$)	e) Pt^{2+} = (NA; $S = 0$)

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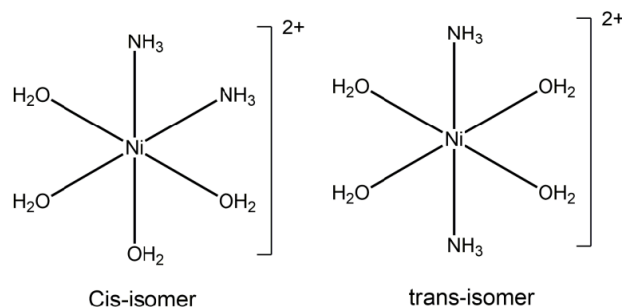
Q-IV.4. Which one would you expect to have a greater magnetic moment: CoCl_4^{2-} or CoI_4^{2-} ? Why?

$[\text{CoI}_4]^{2-}$, because the first excited state is expected to be closer to the ground state compared to $[\text{CoCl}_4]^{2-}$. Hence, the orbital contribution arising from the excited state of $[\text{CoI}_4]^{2-}$ is larger than the same in $[\text{CoCl}_4]^{2-}$.

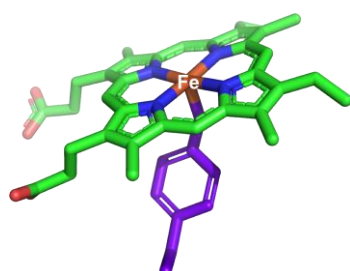
Q-IV.5. 'Y' is a complex of nickel possessing water and ammonia as ligands, but not in equal in number. Complex 'Y' upon treatment with AgNO_3 gives two equivalents of AgCl ; it gives a measured magnetic moment of 2.9 BM. Give the formula of the complex and draw its both the isomeric structures.

- It is given that the complex Y gives two equivalent of AgCl upon reaction with AgNO_3 . Hence this suggests that there are two chloride ligand is outside the coordination sphere.
- Since the water and ammonia ligands are neutral and two halides outside the coordination sphere implies that the metal oxidation state should be +2.
- Complex Y shows mag. Moment value of 2.9 BM corresponds to an octahedral (spin only value) complex.
- As it is stated, water and NH_3 should not be equal in number, the only combination which will give octahedral complex, at the same time which will have two isomer formation for the proposed formula.

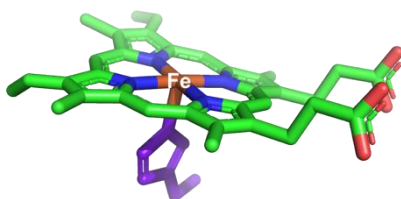
$[\text{Ni}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_2$ or $[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{Cl}_2$



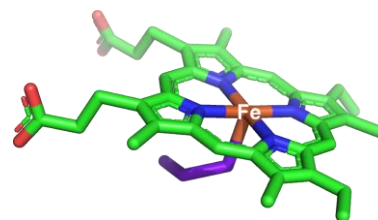
Q-V. 6. The principal difference observed in the metal active site of catalase, peroxidase, and cytochrome P-450 enzymes is the identity of the axial ligand (tyrosine, histidine, and cysteine, respectively, as shown in figure below). How the axial ligand $\rightarrow \text{Fe}(\text{heme})$ σ -donation property varies for these three enzyme active sites? (consider $\text{Fe}(\text{III})$ oxidation state as the resting site).



Catalase
Tyrosine
axial ligand



Peroxidase
Histidine
axial ligand

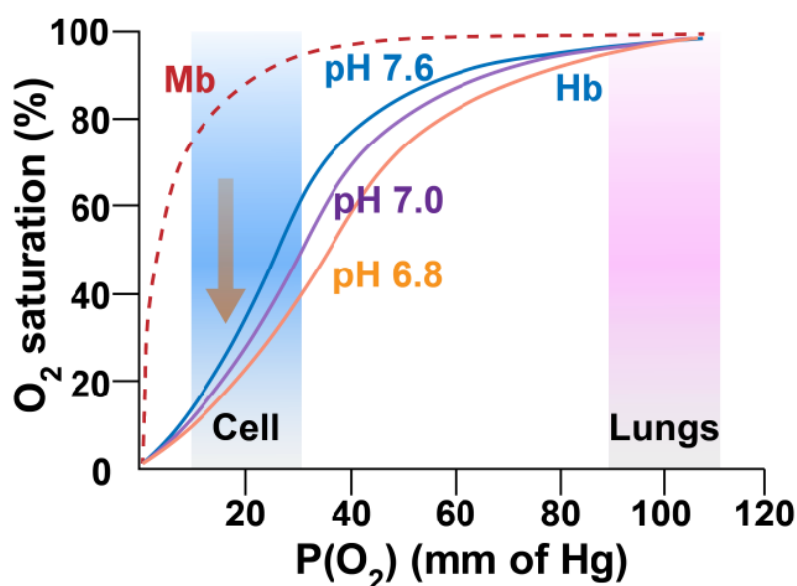


Cytochrome P-450
Cysteine
axial ligand

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Answer: The axial ligand \rightarrow Fe(heme) σ -donation propensity follows the following trend: S(cysteine) \rightarrow Fe(heme) $>$ O(tyrosine) \rightarrow Fe(heme) $>$ N(histidine) \rightarrow Fe(heme). The σ -donation is strongest for the thiolate group present in cysteine due to the involvement of S(3p) orbitals that has significant overlap with Fe(d)-orbitals. Among the rest, the tyrosinate (Ph-O⁻) pushes its electron density strongly towards heme Fe compared to N (histidine) due to the presence of negative charge (N-histidine is neutral here).

Q-V.7. Following is the O₂-binding curve for Hemoglobin (Hb) at pH 6.8, 7.0, and 7.6 along with Myoglobin. If a cell is started to get saturated with CO₂, what will be the response from Hb and Mb?



Answer: As the cell starts to get saturated with CO₂, the cytoplasm will start absorbing it to generate carbonic acid (pK_a ~ 6.4). This will drop the cellular pH. At this condition, The Hb will start to lose O₂ and prefer the tensed deoxy form compared to pH ~ 7 conditions (See the graph). However, the Mb has a negligible effect of such pH-change and will continue to bind the released O₂ strongly. This phenomenon will ensure a surge in cellular O₂ concentration in CO₂-saturated cells (triggered by the pH-change).

Q-V.8. Why the Hemoglobin (Hb) preferably binds O₂ over CO despite better p-back-bonding properties of CO?

Answer: The binding pocket of Hemoglobin (Hb) (i.e., the axial site trans to the proximal histidine) contains a distal histidine ligand originating from the protein scaffold around the heme. The presence of this distal histidine hinders any linear binding for the incoming sixth ligand to the heme-binding pocket and compels a bent binding mode. Such a bent binding mode favours the σ -interaction between heme Fe and O₂ (via its π^* orbital) (see the figure). However, the same is not true for CO molecule, where the extent of overlap between heme Fe and CO (via its σ -symmetric HOMO) is severely hampered (see the figure). Hence, the Hb prefers to bind O₂ over CO (and N₂ and CO₂ too for analogous reasons).

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