

## Tutorial 2

Q1. The magnetic moment of an octahedral Co(II) complex is  $4.0 \mu_B$ . What is its electron configuration?

Answer:

$$\mu = [n(n+2)]^{1/2} \mu_B \Rightarrow 4.0 = [n(n+2)]^{1/2} \Rightarrow n \approx 3$$

A Co(II) complex is  $d^7$ . The two possible configurations are  $t_{2g}^5 e_g^2$  (high spin) with three unpaired electron or  $t_{2g}^6 e_g^1$  (low-spin) with one unpaired electron.

The spin only magnetic moment are  $3.87 \mu_B$  and  $1.73 \mu_B$ , respectively. Therefore the only consistent assignment is the high-spin configuration  $t_{2g}^5 e_g^2$ .

Q2. What is the magnetic moment of  $[\text{CoF}_6]^{3-}$ , assuming that the spin-only formula will apply.

Answer:

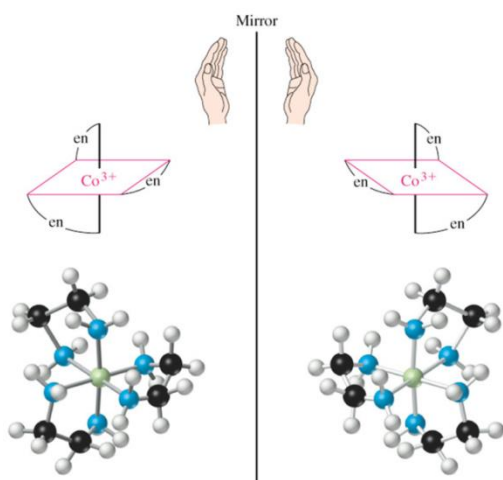
$[\text{CoF}_6]^{3-}$  is high spin Co(III). (you should know this). High-spin Co(III) is  $d^6$  with four unpaired electrons, so  $n = 4$ .

$$\text{We have } \mu_{\text{eff}} = [n(n+2)]^{1/2} = 4.90 \mu_B$$

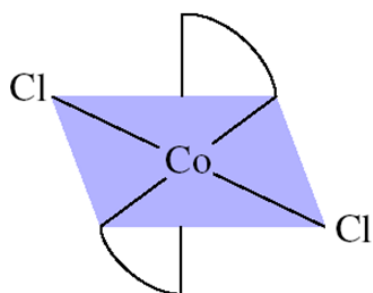
Q3. Two different complexes, one red-orange (**A**) and the other green (**B**), can be isolated from an aqueous solution of  $\text{Co}^{3+}$  containing excess HCl and ethylene diamine (en). The red-orange complex **A** has the empirical formula  $\text{CoCl}_3(\text{en})_3$  while the green complex **B** has the empirical formula  $\text{CoCl}_3(\text{en})_2$ . Addition of excess  $\text{AgNO}_3$  (aq) to an aqueous solution of **A** or **B** produces a white precipitate but **A** produces 3 times as much precipitate as **B** on a molar basis. The red-orange complex **A** can be resolved into a pair of enantiomers while the green complex **B** is not chiral. **Assume  $\text{Co}^{3+}$  has the same coordination number in both complexes.** Propose reasonable structures for both complexes **A** and **B** consistent with these observations and the behaviour of chelate ligands.

Answer: Addition of  $\text{Ag}^+$  precipitates free  $\text{Cl}^-$  so **A** has three free  $\text{Cl}^-$  and **B** only one. en is ethylenediamine and it binds as a bidentate chelate through both amino Nitrogen. For **A** this gives rise to helical chirality in the tris(chelate) as either the  $\Delta$  or  $\Lambda$  forms. For **B**, there must be two bound en and two bound  $\text{Cl}^-$  but since there are no optical isomers, it must mean that this is the trans isomer (cis has no mirror planes and is chiral).

Complex A is  $[\text{Co}(\text{en})_3]\text{Cl}_3$  which will exist as a pair of enantiomers.



Complex B will be *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl (it cannot be the *cis*-isomer because *cis*- will exist as a pair of enantiomers).



Q4. The crystal field splitting energy of a complex is  $2.9 \times 10^{-19}$  J. What wavelength of light (in nm) would be absorbed for a d-d electronic transition corresponding to this splitting?

$$|\Delta E_{\text{electron}}| = E_{\text{photon}} = hc/\lambda$$

$$2.9 \times 10^{-19} \text{ J} = [(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})]/\lambda$$

$$\lambda = 6.849913103 \times 10^{-7} \text{ m} = 680 \text{ nm}$$

Q5. [Ni(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> is paramagnetic while isoelectronic [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> is diamagnetic. Explain in a few words how this could be so.

Answer: Both Ni(II) and Pd(II) have a d<sup>8</sup> configuration. But since Ni(II) complex with a weak field ligand such as NH<sub>3</sub> will be tetrahedral, the electronic configuration will be e<sup>4</sup>t<sub>2</sub><sup>4</sup> resulting in two unpaired electrons. On the other hand, Pd(II) complex will be square planar with no unpaired electrons.

Q6. The value of  $\Delta_o$  in [Mn(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> is 15,800 cm<sup>-1</sup> while the mean pairing energy (P) in this complex is 28,000 cm<sup>-1</sup>. Do you expect this ion to be high or low spin?

Answer: This is a d<sup>4</sup> ion. In this case, you should know that when  $\Delta_o > P$ , a low spin complex will result and when  $\Delta_o < P$  a high spin complex will be observed. Since  $\Delta_o = 15,800 < P = 28,000 \text{ cm}^{-1}$ , a high spin complex will be observed.

Q7. For the following complexes, give the crystal field stabilization energy (in terms of Dq), the spin-only magnetic moment (in Bohr-Magnetons), and predict if the complex will be Jahn-Teller active. If the complex is Jahn-Teller active, indicate the likely nature of the distortion.

Answer:

a. [CoF<sub>6</sub>]<sup>3-</sup>

Co<sup>3+</sup> is d<sup>6</sup> in a weak field so the stabilization energy is -4Dq. There are 4 unpaired electrons so  $\mu = [4(4+2)]^{1/2} = 4.9 \mu_B$ . d<sup>6</sup> in a weak field is Jahn-Teller active and should display axial compression.

b. [V(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>

V<sup>3+</sup> is d<sup>2</sup> in a weak field so the stabilization energy is -8Dq. There are 2 unpaired electrons so  $\mu = [2(2+2)]^{1/2} = 2.8 \mu_B$ . d<sup>2</sup> in a weak field is Jahn-Teller active and should display axial elongation.

c. [Mn(CN)<sub>6</sub>]<sup>3-</sup>

$\text{Mn}^{3+}$  is  $d^4$  in a strong field so the stabilization energy is  $-16Dq$ . There are 2 unpaired electrons so  $\mu = [2(2+2)]^{1/2} = 2.8 \mu_B$ .  $d^4$  in a strong field is Jahn-Teller active and should display axial compression.

d.  $[\text{Cr}(\text{H}_2\text{O})_3(\text{CN})_3]^-$

$\text{Cr}^{2+}$  is  $d^4$  in a strong field (cyanide is a very strong ligand, water is near the change over from weak to strong, so the stronger ligands dominate) so the stabilization energy is  $-16Dq$ . There are 2 unpaired electrons so  $\mu = [2(2+2)]^{1/2} = 2.8 \mu_B$ .  $d^4$  in a strong field is Jahn-Teller active and should display axial compression.