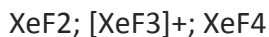


Answer on Question #76764, Chemistry / Inorganic Chemistry

1 . Answer ALL parts a) — c).

a) Use the principles of Valence Shell Electron Pair Repulsion (VSEPR) to predict the structures of the following species.



b) Some of the halogens form oxo-acids in which their oxidation state is +7. Comment briefly on the observations that:

i) fluorine does not form a compound of this type;

ii) the compounds of iodine (H_5IO_6) and chlorine (HClO_4) have different structures.

2 . Draw the structure of the following coordination compounds and determine the oxidation state, d orbital electronic configuration, (t_{2g} eg" Or e_g " configuration and the spin only magnetic moment of the metal atom.

i) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

ii) $[\text{Fe}(\text{ox})_3]^{3-}$, ox = oxalate dianion, $\text{C}_2\text{O}_4^{2-}$

iii) $[\text{Ni}(\text{en})_3]^{2+}$, en = 1,2-diaminoethane

Solution

1) a) Use the principles of Valence Shell Electron Pair Repulsion (VSEPR) to predict the structures of the following species.



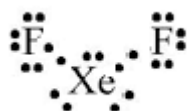
a) The main principle VSEPR theory is that the geometry of the molecule is determined by the repulsions among the electron pairs in the valence shell of its central atom. We should determine the number of bonding and lone pairs to establish the molecular geometry. These electron pairs of the valence shell must be at maximum distances from each other.

- XeF_2

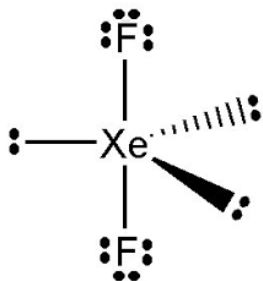
Find the number of electron pairs around central atom:

Xe has 8 valence electrons: $[\text{Kr}]4d^{10}5s^25p^6$, every atom of F has 7 valence electrons: $[\text{He}]2s^22p^5$, as we have two atoms of F the number of valence electrons should be multiplied by two ($7 \cdot 2 = 14$). Total number is 22.

Lewis structure of XeF_2 is :



There are two bonding pairs and three lone pairs around central atom of Xe
Structure of XeF_2 in VSEPR theory is:



Molecular geometry: Linear.

- $[\text{XeF}_3]^+$

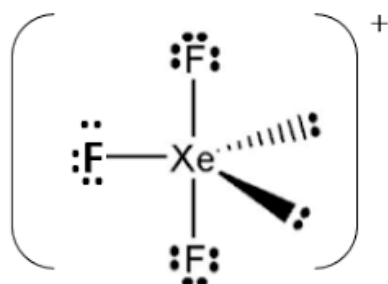
Find the number of electron pairs around central atom:

Xe has 8 valence electrons: $[\text{Kr}]4d^{10}5s^25p^6$, every atom of F has 7 valence electrons: $[\text{He}]2s^22p^5$, as we have three atoms of F the number of valence electrons should be multiplied by three ($7 \cdot 3 = 21$). The molecule $[\text{XeF}_3]^+$ has positive charge, that means we should take away one electron. Total number is $8 + 7 \cdot 3 - 1 = 28$.

Lewis structure of $[\text{XeF}_3]^+$ is :



There are three bonding pairs and two lone pairs around central atom of Xe
Structure of $[\text{XeF}_3]^+$ in VSEPR theory is:



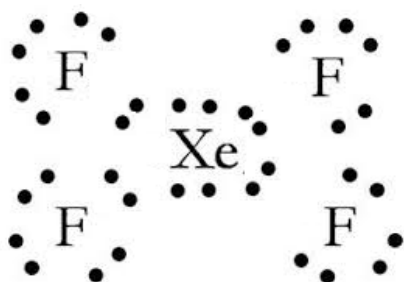
Molecular geometry is: T-shape

- XeF_4

Find the number of electron pairs around central atom:

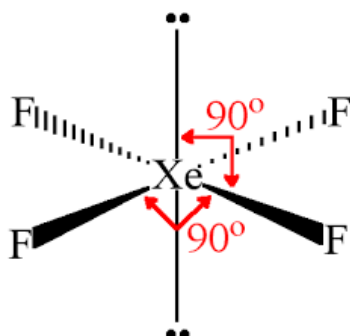
Xe has 8 valence electrons: $[\text{Kr}]4d^{10}5s^25p^6$, every atom of F has 7 valence electrons: $[\text{He}]2s^22p^5$, as we have four atoms of F the number of valence electrons should be multiplied by four ($7 \cdot 4 = 28$). Total number is 36.

Lewis structure of XeF_4 is :



There are four bonding pairs and two lone pairs around central atom of Xe

Structure of XeF_4 in VSEPR theory is:

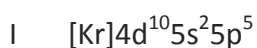
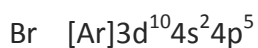


Molecular geometry is: Square planar.

- b) Some of the halogens form oxo-acids in which their oxidation state is +7. Comment briefly on the observations that:
- i) fluorine does not form a compound of this type;
 - ii) the compounds of iodine (H_5IO_6) and chlorine (HClO_4) have different structures

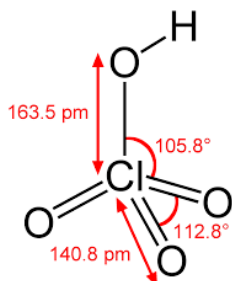
To answer this question we should take into account electronic structures of halogens and their radii.

Electronic structures:

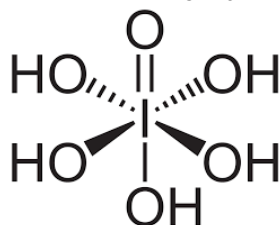


i) Fluorine can not form oxo-acids in which its oxidation state is +7, as to have such an oxidation state atom of F should come up in excited state and have 7 lone electrons. But fluorine has 2 energy levels, where only s and p orbitals are allowed, there are no d orbitals where lone electrons can be placed. The other halogens have vacant d-orbitals, where lone electrons can be placed. For this reason Cl, Br and I can have oxidation state +7.

ii) Structure of HClO_4



Structure of H_5IO_6



Iodine can form both HIO_4 and H_5IO_6 structures where its oxidation state is +7. The last acid H_5IO_6 can be formed due to the increase of iodine radius in comparison with radii of Cl and Br and consequently increase of coordination number from 4 to 6.

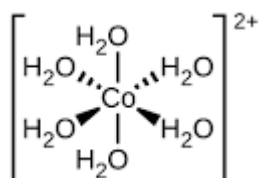
2. Draw the structure of the following coordination compounds and determine the oxidation state, d orbital electronic configuration, (t_{2g} e_g or e_g t_{2g} configuration and the spin only magnetic moment of the metal atom.

i) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

ii) $[\text{Fe}(\text{ox})_3]^{3-}$, ox = oxalate dianion, $\text{C}_2\text{O}_4^{2-}$

iii) $[\text{Ni}(\text{en})_3]^{2+}$, en = 1,2-diaminoethane

i) Structure of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$



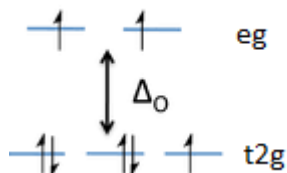
The electron configuration of Cobalt is : $[\text{Ar}] 3d^7 4s^2$

Oxidation state of cobalt in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is Co^{2+} , as H_2O ligands have no charge.

d^7 electronic configuration, as atom of Co loses two electrons to become an ion Co^{2+} .

The complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ has an octahedral shape. H_2O is a weak field ligand, consequently, complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is high spin, splitting energy Δ_o is small.

Splitting d-orbital diagram of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is: $t_{2g}^5 e_g^2$



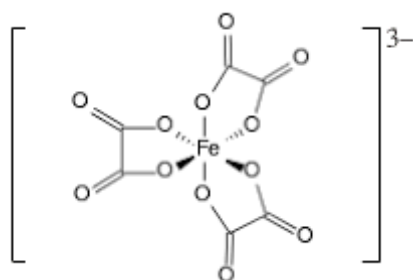
This complex is paramagnetic as it has three lone electrons.

Find the spin-only magnetic moment of this complex using formula, based on the number of unpaired electrons n :

$$\mu_{so} = \sqrt{n(n + 2)}$$

For complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ $\mu_{so} = \sqrt{3(3 + 2)} = \sqrt{15} = 3.87 \mu_B$

ii) Structure of $[\text{Fe}(\text{ox})_3]^{3-}$, ox = oxalate dianion, $\text{C}_2\text{O}_4^{2-}$



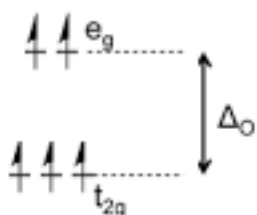
The electron configuration of Iron is : $[\text{Ar}] 3d^6 4s^2$

Oxidation state of Iron in $[\text{Fe}(\text{ox})_3]^{3-}$ is Fe^{3+} , as each of , $\text{C}_2\text{O}_4^{2-}$ ligands has two negative charges and charge of the complex is -3: $(+3+3 \cdot (-2)) = -3$.

d^5 electronic configuration, as atom of Fe loses three electrons to become an ion Fe^{3+} .

The complex $[\text{Fe}(\text{ox})_3]^{3-}$ has an octahedral shape. $\text{C}_2\text{O}_4^{2-}$ or ox is a weak field ligand, consequently, complex $\text{C}_2\text{O}_4^{2-}$ is high spin, splitting energy Δ_o is small.

Splitting d-orbital diagram of $[\text{Fe}(\text{ox})_3]^{3-}$ is: $t_{2g}^3 e_g^2$

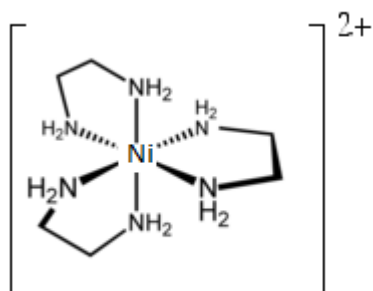


This complex is paramagnetic as it has five lone electrons.

$$\mu_{so} = \sqrt{n(n+2)}$$

For complex $[\text{Fe}(\text{ox})_3]^{3-}$ $\mu_{so} = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \mu_B$

iii) Structure of $[\text{Ni}(\text{en})_3]^{2+}$, en = 1,2-diaminoethane



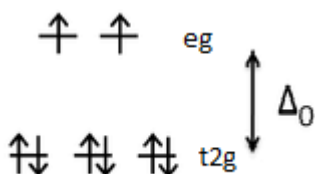
The electron configuration of Nickel is : $[\text{Ar}] 3d^8 4s^2$

Oxidation state of Nickel in $[\text{Ni}(\text{en})_3]^{2+}$, is Ni^{2+} , as en ligands have no charge.

d^8 electronic configuration, as atom of Ni loses two electrons to become an ion Ni^{2+} .

The complex $[\text{Ni}(\text{en})_3]^{2+}$ has an octahedral shape, en is a strong field ligand, but the appropriate crystal field diagram shows that only one configuration is possible irrespective of the strength of the ligand field.

Splitting d-orbital diagram of $[\text{Ni}(\text{en})_3]^{2+}$ is: $t_{2g}^6 e_g^2$



This complex is paramagnetic as it has at two lone electrons.

$$\mu_{so} = \sqrt{n(n+2)}$$

For complex $[\text{Ni}(\text{en})_3]^{2+}$ $\mu_{so} = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \mu_B$