Inorganic Chemistry I

I－a Answer the following questions regarding element families.

（1） The atomic numbers of the carbon family elements are 6, 14, 32, 50, and 82. Write down chemical symbol and ground state electronic configuration for each atom according to the example.

[Example] $_{31}Ga\ (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}(4s)^2(4p)^1$ or $_{31}Ga\ [_{18}Ar](3d)^{10}(4s)^2(4p)^1$

（2） Write down ground state electronic configuration for an element with atomic number 113, nihonium (Nh). Also, which family does this element belong to?

I－b Answer the following questions regarding VSEPR (valence-shell electron pair repulsion) model.

（1） Which is stronger in electron pair repulsion, lone electron pair or bonding electron pair? Also, explain the reason.

（2） How many lone electron pairs and how many bonding electron pairs do CH_4, NH_3, and H_2O molecules have?

（3） Which is larger or smaller in bond angle, CH_4, NH_3, or H_2O ? Also, explain the reason.

I－c Answer the following questions regarding the molecular orbital (MO) model.

（1） Carbon dioxide (CO_2) and nitrogen dioxide (NO_2) have π -symmetry bonding, non-bonding, and anti-bonding molecular orbitals. Draw these molecular orbitals in outline.

（2） How many π -electrons does CO_2 have ?

（3） CO_2 has a linear structure, and its isoelectronic nitronium ion NO_2^+ is also linear. Explain the reason from the viewpoint of π -symmetry molecular orbitals.

（4） NO_2 has an additional electron to CO_2 and NO_2^+. If NO_2 is linear, an anti-bonding π -symmetry orbital is occupied by this unpaired electron. If so, NO_2 can be more stable for a bent structure. Explain the reason.

Inorganic Chemistry II

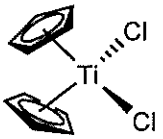
II — a Answer the questions for the following complexes [(i) ~ (v)]. Each metal complex is a monomer. Here, bpy = 2,2'-bipyridine.

(i) $[Co(CN)_2(NH_3)_4]Cl$

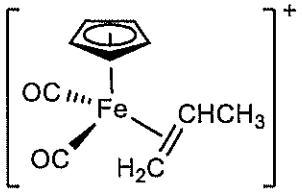
(ii) $RuCl(CO)H(PPh_3)_3$

(iii) $Pt(bpy)(CH_3)_2$

(iv)



(v)



(1) Answer the number of valence electrons by using the electron counting methods which are used in the 18-electron rule. Show the method you used for the valence electron count for each complex.

(2) Answer the oxidation state of the metal center and the number of *d*-electrons for each complex.

II — b Answer the following questions.

(1) Draw all of the possible stereoisomers for the following complexes [(i) ~ (iii)]. The rotational isomers are not considered. Each metal complex is a monomer.

(i) $Ir(CO)H(PPh_3)_2$

(ii) $[RhCl_2(NH_3)_4]^+$

(iii) $CrCl_3(H_2O)_3$

(2) Which of the following complexes [(i) ~ (iv)] can have enantiomers? Here, en = $H_2NCH_2CH_2NH_2$, dien = $NH(C_2H_4NH_2)_2$, and ox = $C_2O_4^{2-}$.

(i) $[Co(H_2O)(NH_3)_5]^{3+}$, (ii) $[CoCl_2(en)_2]^+$, (iii) $[PtCl(dien)]^+$, (iv) $[Cr(ox)_3]^{3-}$

Ⅱ－c　Answer the following questions.

The following metal complexes [(i) and (ii)] are six-coordinate Mn (II) complexes having an octahedral metal center.

(i)　$[Mn(H_2O)_6]^{2+}$ (the magnetic moment is $5.9\mu_B$ at 300 K)

(ii)　$[Mn(CN)_6]^{4-}$ (the magnetic moment is $3.2\mu_B$ at 300 K)

（1）Draw the *d*-orbital energy level diagrams for the complexes (i) and (ii), and label each *d*-orbital (d_{xy}, d_{yz}, d_{zx}, d_{z^2}, $d_{x^2-y^2}$). Be sure to add electrons in the diagram. Use "↑" and "↓" to represent electrons in the diagram.

（2）Which complex has the larger ligand-field splitting parameter (Δ_o), the complex (i) or (ii) ? Explain the reason for your answer.

（3）The molar absorption coefficient of the *d-d* transition for the complex (i) is extremely smaller than that for the complex (ii). Explain briefly the reason why the intensity of the *d-d* transition is different between these complexes, by considering the *d*-orbital energy level diagram.

Ⅱ－d　Answer the following questions.

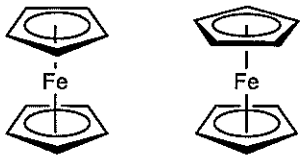
$[Cu(H_2O)_6]^{2+}$ is a complex with distorted octahedral geometry. In this complex, six Cu-O bonds exist and two Cu-O bonds are longer than the remaining four Cu-O bonds.

（1）Draw the structure of $[Cu(H_2O)_6]^{2+}$ with showing the position of two longer Cu-O bonds.

（2）Explain briefly the reason why $[Cu(H_2O)_6]^{2+}$ has a distorted octahedral metal center, by considering the *d*-orbital energy level diagram.

Ⅱ－e　Answer the following questions.

Ferrocene ($(\eta^5\text{-}C_5H_5)_2Fe$) can have the following two conformational isomers [(i) staggered form and (ii) eclipsed form].



(i)　(ii)

（1）Determine the point group for the conformational isomers (i) and (ii).

（2）Explain briefly the reason why the one-electron reduced complex of ferrocene ($[(\eta^5\text{-}C_5H_5)_2Fe]^+$) is a good one-electron oxidant and cobaltocene ($(\eta^5\text{-}C_5H_5)_2Co$) is a good one-electron reductant, by considering the change of the number of valence electrons upon redox reactions.