Inorganic Chemistry I

I − a Answer the following questions regarding alkaline earth metals.

(1) Write down the ground state electronic configurations for magnesium (Mg), calcium (Ca), and barium (Ba) according to the example.

[Example] $_{14}Si\ (1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$ or $_{14}Si\ [_{10}Ne](3s)^2(3p)^2$

(2) Which reactant acts as an acid in each reaction [(i) and (ii)] ? Also, which term best describes the acid, Brønsted-Lowry acid or Lewis acid?

(i) $2NaCl + BeCl_2 \rightarrow Na_2[BeCl_4]$
(ii) $Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$

(3) Both calcium chloride ($CaCl_2$) and calcium hydride (CaH_2) are used as drying agents. How do they function as drying agents?

I − b Consider the structures of the following molecules and ion, (i) ~ (iii), based on the valence-shell electron pair repulsion (VSEPR) model, and draw the structures with showing spatial arrangement of each atom clearly. In case that the central atom has lone-pair electrons, show the direction of each lone pair in the structure. Also, answer the point group for each molecule or ion, (i) ~ (iii).

(i) XeF_4
(ii) $SnCl_2$
(iii) SbF_6^-

I − c Answer the following questions regarding allotropes of carbon.

(1) Graphite and diamond are two common allotropes of carbon. Explain the difference in structure by drawing the structures of these two allotropes.

(2) The hardness and electric conductivity of graphite are significantly different from those of diamond. Explain the reason briefly.

(3) Give another allotrope of carbon, and explain the structure of the allotrope briefly.

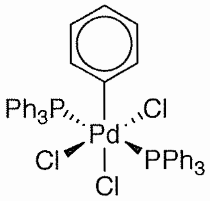
Inorganic Chemistry II

II－a Answer the questions for the following organometallic complexes [(i) ~ (v)] having group 6 atom (Cr, Mo, W), group 7 atom (Mn) and group 10 atom (Pd).

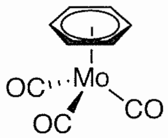
(i) $W(CH_3)_6$

(ii) $[Mn(CO)_5]^-$

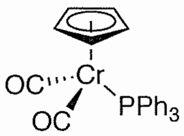
(iii)



(iv)



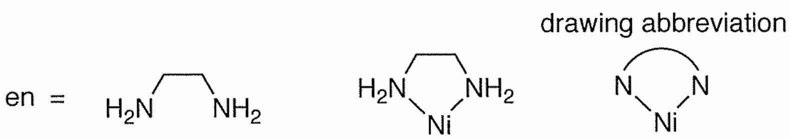
(v)



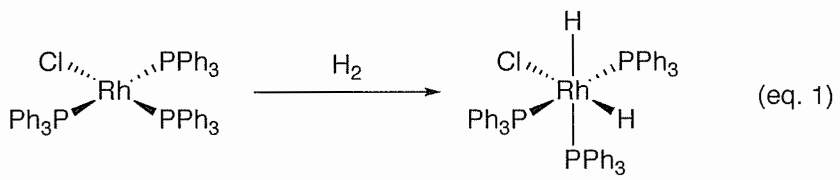
(1) Answer the oxidation state of the metal atom and the number of *d*-electrons for each complex.

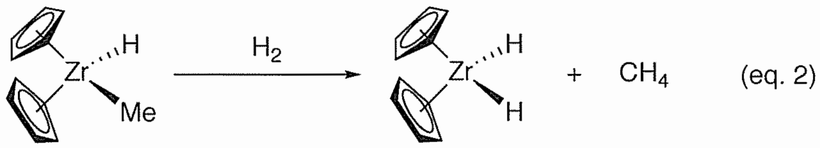
(2) Answer the number of valence electrons by using the electron counting methods which are used in the 18-electron rule. Show the method you used for the valence electron count for each complex.

II－b For the $[Ni(en)_3]^{2+}$ complex, there are two stereoisomers that can be easily interconverted. Draw these two stereoisomers. Also, explain the mechanism for the interconversion. Here, the en ligand may be abbreviated as follows, when you draw stereoisomers.



II－c　Answer the following questions regarding the reactions of Rh (group 9) and Zr (group 4).





(1)　The reaction shown in eq. 1 is known as an oxidative addition reaction.　Answer the reason why the reaction is called as "oxidative".

(2)　The reaction shown in eq. 2 is proposed to proceed via σ-bond metathesis.　Draw the structure of a transition state leading to the product.

(3)　In contrast to the Rh complex shown in eq. 1, the Zr complex does not undergo an oxidative addition reaction upon the reaction with hydrogen molecule shown in eq. 2.　Explain the reason for this briefly.

II－d　Answer the following questions regarding d^6 Co^{III} complexes.

(1)　Draw the *d*-orbital energy diagram for the six-coordinate diamagnetic $[Co^{III}(NH_3)_6]^{3+}$ complex of an octahedral geometry, according to the crystal field theory.　Label each *d*-orbital (d_{xy}, d_{yz}, d_{xz}, d_{z2}, d_{x2-y2}).　Use "↑" and "↓" to represent electrons in the diagram.

(2)　The $[Co^{III}(NH_3)_6]^{3+}$ complex shows three absorption bands of different intensity in the UV-vis region, namely the transitions A ($\varepsilon_{max} = 60 \sim 80\ M^{-1}\ cm^{-1}$), B ($\varepsilon_{max} = \sim 2\ M^{-1}\ cm^{-1}$) and C ($\varepsilon_{max} = \sim 20000\ M^{-1}\ cm^{-1}$).　Assign the transitions A, B and C, respectively, from the following 6 choices.

ligand-to-metal charge transfer transition, metal-to-ligand charge transfer transition, π- π* transition, spin-allowed d-d transition, spin-forbidden d-d transition, intervalence charge transfer transition

(3)　The $[Co^{III}Cl(NH_3)_5]^{3+}$ complex is prepared by exchanging one of the NH_3 ligands in $[Co^{III}(NH_3)_6]^{3+}$ with a Cl ligand.　Explain the effect of the Cl ligand on the orbital energies of d_{z2} and d_{yz} / d_{xz}, respectively.　Here, the Cl ligand is positioned on the z axis.