1996 Inorganic Examination (total 100 points)

1. In the development of quantum mechanics (to describe the structure of atoms), three persons; Werner Heisberg, Louis De Broglie and Erwin Schrodinger, have more significant contribution. Briefly describe the contents of their theories (15 points).

2. How might one distinguish between the following isomers? (9 points).

(a) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$.
(b) $[Co(NH_3)_3(NO_2)_3]$ and $[Co(NH_3)_6][Co(NO_2)_6]$.
(c) cis- and trans-$[Co(Cl)_2(en)_2]Cl$.

3. Draw a simple qualitative MO (molecular orbital) diagram for $Mo(CO)_6$ or $Mo(CN)_6^{n-}$ compound, and also explain that the metal binds to C atom, not O atom. (assuming the structure of the complexes is a perfect octahedron) (10 points)

4. Why are layer structures such as those of $CdCl_2$ and CdI_2 usually not encountered for metal fluoride or compounds of the most active metals? (5 points)

5. Give the bond order and the number of unpaired electrons for Be_2^+, B_2^+, C_2^+, O_2^+, and O_2^-. (5 points)

6. The intensity of an infrared absorption is proportional to the change in the dipole moment occurring during the vibration. The asymmetric stretching vibration in IHI^- is far more intense than that found for the stretching vibration of HI. Please give a reasonable explanation. (6 points)

7. Please calculate the LFSE values of transition metal complexes with electronic configuration of d^6 -octahedron in term of high- and low-field ligands. (6 points)

8. Replacement of a ligand by OH^- is called base hydrolysis. In fact, it was argued for some time that base hydrolysis provided an example of an A (Association) reaction involving rate-determining attack by OH^-. However it would be extremely suprising if OH^- were the only nucleophile in aqueous solution capable of attack. Please propose a reasonable mechanism for the following reaction. (6 points)

$$[Co(NH_3)_5Cl]^{2+} + OH^- \text{ ----------> } [Co(NH_3)_5(OH)]^{2+} + Cl$$

9. Propose a mechanism for the following incorporation reaction. (5 points)

$$S_2O_4^{2-} + {}^*SO_2 \text{ <----------> } O_2S{}^*SO_2^{2-} + SO_2$$

10. In compounds containing terminal carbonyls, the electron-donor abilities of the metal and other ligands are reflected in the CO stretching vibration frequencies υ_{CO}. Given the following IR data, please rationalize the observed trend in frequencies. (7 points)

$Ti(CO)_6^{2-}$	1748 cm^{-1}
$V(CO)_6^-$	1858 cm^{-1}
$Cr(CO)_6$	1984 cm^{-1}
$Mn(CO)_6^+$	2094 cm^{-1}
CO	2143 cm^{-1}

11. Give the valence electron count for the following species.(16 points; 2 each. show the calculation for credit)

(a) $CpMo(CO)_3(\eta^1\text{-}C_3H_5)$ (b) $Ir(PPh_3)_2(CO)Cl(\eta^2\text{-}C_3H_6)$ (c) $Co_2(\mu\text{-}CO)_2(CO)_6$

(d) $Mn(CO)_5CH_2C_6H_5$ (e) $HIRh(CO)_5$ (f) $Ru_3(CO)_{12}$ (g) $[\eta^4\text{-}COD)Ru(\mu\text{-}Cl)_2]_2$

(h) $CpCr(NO)_2Me$

12. Propose a mechanism for the stoichiometric decarbonylation of $C_6H_5CH_2C(O)Cl$ by $Rh(PPh_3)_3Cl$ giving benzyl chloride. Keep in mind the 16- and 18-electron rule. (6 points)

13. Solution of triethylamine in $POCl_3$ as solvent becomes conducting. Please explain this phenomenon. (4 points)