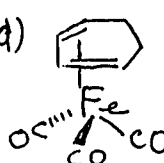


- Write the chemical formula for each of the following: (8%)
 - thiocyanate ion
 - boric acid
 - trisilane
 - hexaquaachromium trichloride.
- Which of the following gas-phase reactions can proceed spontaneously? Explain. (4%)
 - $Kr + He^+ \rightarrow Kr^+ + He$
 - $Si + Cl^+ \rightarrow Si^+ + Cl$
- Explain the observation that the energy difference between the $^2S_{1/2}$ state of $1s^2 2s^1$ and the $^2P_{1/2}$ state of $1s^2 2p^1$ for Li is 14904 cm^{-1} , whereas for Li^{2+} the $^2S_{1/2}$ state of $2s^1$ and the $^2P_{1/2}$ state of $2p^1$ differ by only 2.4 cm^{-1} . (6%)
- Which of the following in each pair will have the larger bond angle? Why? (8%)
 - CH_4, NH_3
 - OF_2, OCl_2
 - NH_3, NF_3
 - PH_3, NH_3
- The bond dissociation energy of C_2 (599 kJ/mol) decreases slightly on forming C_2^+ (513 kJ/mol), and increases greatly on forming C_2^- (818 kJ/mol). Why? (6%)
- Explain why the anhydrous acid $HICl_4$ cannot be isolated, but the crystalline hydrate $HICl_4 \cdot 4H_2O$ may be obtained from ICl_3 in aqueous HCl. (5%)
- Treatment of $CrCl_3(s)$ with $NH_3(l)$ yields very largely the complex $[Cr(NH_3)_5Cl]Cl_2(s)$, but if a small quantity of elemental potassium is first dissolved in the $NH_3(l)$, the product is largely $[Cr(NH_3)_6]Cl_3$. Explain by giving a possible mechanism. (6%)
- Determine the point group of the following: (8%)
 - CH_3Cl
 - CH_2Cl_2
 - CH_2BrCl
 - $XeOF_4$
 - BrF_3
 - NSF_3
 - $B_3N_3H_6$
 - cis- $[CoF_4Cl_2]^{3-}$
- Explain the following: (18%)
 - The Ag^+ ion is larger in a square planar environment than it is in a tetrahedral one. For Ni^{2+} the reverse is true.
 - $Ni(CN)_4^{2-}$ is a square planar complex while $NiCl_4^{2-}$ is a tetrahedral complex.

- (c) $\text{Fe}(\text{NO}_2)_6^{4-}$ is an inert complex while FeF_6^{4-} is labile.
10. How many d-d bands would you expect for a d^1 ion in an environment with (a) tetrahedral symmetry, T_d ; (b) trigonal symmetry, C_{3v} , derived from T_d by elongation along one C_3 axis? Explain. (6%).
11. Describe the differences between 4f and 5f orbitals. (5%).
12. Predict reasonable products for the following reactions. (5%)
- (a) $\text{Mm}_2(\text{CO})_{10} + \text{H}_2 \longrightarrow ?$ (b) $\text{NaC}_5\text{H}_5 + \text{Fe}(\text{CO})_5 \longrightarrow ?$
- (c) $(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{PPh}_3)(\text{CH}_2\text{PR}) + \text{HCl} \longrightarrow ?$
- (d)  + $\text{PPh}_3 \xrightarrow{\text{Me}_3\text{NO}} ?$ (e) $(\pi\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3) + \text{P}(\text{CH}_3)_3 \longrightarrow ?$
13. Which of the two complexes has the lower energy CO stretching frequency in the IR spectrum? (5%)
- (a) $[\text{Mo}(\text{CO})_5\text{Cl}]^-$ or $\text{Tc}(\text{CO})_5\text{Cl}$ (b) $\text{Fe}(\text{CO})_5$ or $\text{Fe}(\text{CO})_4\text{Cl}_2$ (c) $\text{W}(\text{CO})_6$ or $\text{W}(\text{CO})_4(\text{PPh}_3)_2$
- (d) $\text{Mo}(\text{CO})_4(\text{PMe}_3)_2$ or $\text{Mo}(\text{CO})_4(\text{PF}_3)_2$ (e) $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-Br}$ or $[(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]^-$.
14. Treatment of $\text{CH}_3\text{Mn}(\text{CO})_5$ with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ gives a product which has the formula, $\text{C}_5\text{H}_3\text{MnO}_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$. The IR spectrum shows ν_{CO} at 1999, 1916 (broad), and 1588 cm^{-1} . The $^1\text{H NMR}$ spectrum shows, in addition to phenyl protons, a singlet at δ 2.34 and a twelve line pattern at about δ 4.60. (a) Deduce the two possible products (b) Use the physical data to determine the real product. (6%)
15. In 1983, Bergman reported that n-pentane can add oxidatively with $(\pi\text{-C}_5\text{Me}_5)\text{Ir}(\text{PMe}_3)$, the reductive-elimination product of $(\pi\text{-C}_5\text{Me}_5)\text{Ir}(\text{PMe}_3)_2\text{H}_2$, to give four different products. Write the structures of these products. (4%)