

無機化學

國立成功大學75學年度化學研究所考試(試題)共兩頁 第一頁

1. (a) Write out the electron configuration of manganese atom (25Mn) (2%)  
 (b) Using Slater's rules, calculate the effective nuclear charge of a 3d electron in Mn. (3%)
2. The order of acidity of boron halides is  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ . Suggest possible explanations. (4%)
3. Draw qualitatively the nitrogen 1s photoelectron spectrum of  $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{NO}_3$  ( $\text{en} = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) and give explanation. (5%)
4. Using "bent bond" to describe the triple bond in the acetylene molecule. (3%)
5. Name the following compounds in English: (a)  $\text{Cs}^+\text{Au}^-$  (b)  $\text{B}_4\text{H}_{10}$  (4%)
6. Which one in each of the following pairs has the higher IR absorption frequency for C=O bond: (a)  or  (b)  $[\text{Mn}(\text{CO})_6]^+$  or  $[\text{V}(\text{CO})_6]^-$ ? and give brief explanation. (6%)
7. Given the normalized wave functions of the three  $sp^2$  hybrid orbitals  
 $\psi_1 = \frac{1}{\sqrt{3}}\psi_s + \frac{\sqrt{2}}{\sqrt{3}}\psi_{px} + a\psi_{py}$ ,  $\psi_2 = \frac{1}{\sqrt{3}}\psi_s - b\psi_{px} + c\psi_{py}$ ,  $\psi_3 = \frac{1}{\sqrt{3}}\psi_s - b\psi_{px} - c\psi_{py}$   
 Calculate a, b, and c. ( $a \geq 0, b \geq 0, c \geq 0$ ) (3%)
8. Balance the following redox reactions:  
 (a)  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CO}_2 + \text{Cr}^{3+}$  (acidic solution)  
 (b)  $\text{MnO}_4^- + \text{NO}_2^- \rightarrow \text{MnO}_2(s) + \text{NO}_3^-$  (basic solution) (6%)
9. Give brief explanations for the following observations.  
 (a)  $\text{Fe}(\text{NO}_2)_6^{4-}$  is an inert complex while  $\text{FeF}_6^{4-}$  is labile.  
 (b) The  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ion is pink while the  $\text{CoCl}_4^{2-}$  ion is blue.  
 (c)  $\text{SiCl}_4$  is more easily hydrolyzed than  $\text{CCl}_4$ .  
 (d) Trisilylamine is planar and is a very weak base. (12%)
10. The absorption band in the visible spectrum of  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  is of low intensity. It is somewhat broad and unsymmetrical. Explain these observations. (6%)
11. Explain how to differentiate experimentally between members of each pair of the following compounds. Describe two or more methods in addition to the X-ray diffraction.  
 (a)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  (b) cis- and trans-  $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$   
 (c)  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$  and  $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$  (9%)
12. Complete the following equations: (6%)  
 (a)  $\text{Ag}^+ + \text{N}_3^- \xrightarrow{\text{H}_2\text{O}}$  (b)  $\text{PCl}_5 + \text{H}_2\text{O} \rightarrow$  (c)  $\text{B}_3\text{N}_3\text{H}_6 + 3\text{HCl} \rightarrow$
13. Assign term symbols for  $2p^13p^1$  electron configuration. (6%)
14. Explain why HBr and HI are prepared from protonation of NaBr and NaI, respectively, with  $\text{H}_3\text{PO}_4$  but not with  $\text{H}_2\text{SO}_4$ . (3%)
15. Explain why N,N'-dimethylformamide,  $\text{HCONMe}_2$ , in  $(\text{HCONMe}_2)\text{Mo}(\text{CO})_5$  is an O-donor rather than a N-donor? (3%)

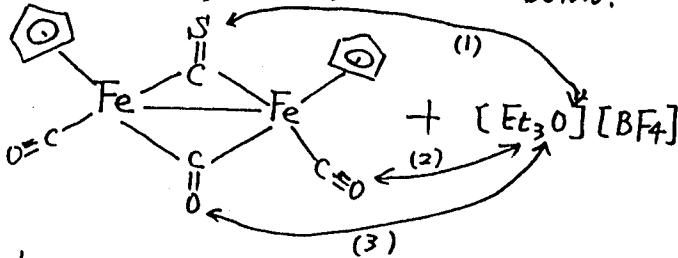
(總計第二頁)

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第二頁

16. Explain why  $(\eta^6\text{C}_6\text{H}_6)_2\text{Cr}$  can not be prepared from  $\text{Cr}(\text{CO})_6$  and excess benzene at high temperature. (3%)
17. Explain why there are many carbonylate anions,  $\text{M}(\text{CO})_x^{y-}$ ,  $y=1, 2, 3$ ;  $x=4, 5, 6$ , whereas there is so far no isocyanide anion,  $\text{M}(\text{CNR})_x^{y-}$ , been found. (4%)
18. There are three possible reaction routes between  $\text{cis}-(\eta^5\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\text{Li}_2-\text{CO})(\text{Li}_2-\text{CS})$  and  $[\text{Et}_3\text{O}]^+[\text{BF}_4]^-$  as shown below.



Which route is the most possible? Explain your choice and write the predicted product. (6%)

19. It was found that the reaction between  $\text{BrMn}(\text{CO})_5$  and  $\text{CH}_3\text{Li}$  gives  $\text{cis-BrMn}(\text{CO})_4(\text{C}-\overset{\text{O}}{\text{C}}\text{H}_3)\text{Li}$ ,  $\begin{array}{c} \text{OC} \\ | \\ \text{OC}-\overset{\text{CO}}{\text{Mn}}-\text{Br} \\ | \\ \text{OC} \end{array}$ .
- (a) Explain why the reaction can not give a substitution product  $\text{CH}_3\text{Mn}(\text{CO})_5$ .  
 (b) Explain why  $\text{trans-BrMn}(\text{CO})_4(\text{C}-\overset{\text{O}}{\text{C}}\text{H}_3)\text{Li}$  is not obtained. (6%)