國立成功大學 106 學年度碩士班招生考試試題

系　　所：化學系

考試科目：無機化學

考試日期：0214，節次：3

※ 考生請注意：本試題不可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

一、選擇題：(60 分，每題 3 分)

1. Predict number of radial node(s) and angular nodal planes of a 4p orbital, respectively.
(A) 2, 1　(B) 3, 0　(C) 3, 1　(D) 2, 2

2. Which atom has the higher electronegativity by Mulliken's definition [χ_M = ½(IE+EA), IE: ionization energy; EA: electron affinity]? (A) O　(B) F　(C) Ne　(D) Cl

3. Decide the point group of 1,2-dichloroethane (staggered anti-conformation).
(A) C_{2v}　(B) C_{2h}　(C) D_{2h}　(D) D_{2d}

4. Decide the point group of a twisted ferrocene $Fe(C_5H_5)_2$. (A) C_5　(B) C_{5v}　(C) D_5　(D) D_{5d}

5. Which of the following bases has the largest affinity in gas phase?
(A) CH_3O^-　(B) $C_2H_5O^-$　(C) *i*-Pr-O^-　(D) *t*-Bu-O^-

6. Which of pentafluorides forming superacids in HSO_3F has the highest acidity?
(A) SbF_5　(B) NbF_5　(C) AsF_5　(D) PF_5

7. Which of oxides is likely to show p-type extrinsic semiconductor?
(A) MgO　(B) MnO　(C) CuO　(D) ZnO

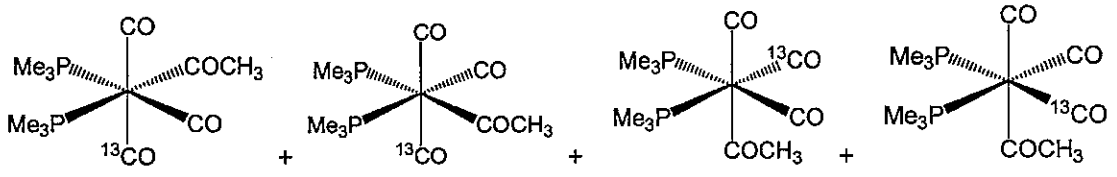
8. Which has the smallest band gap? (A) Si　(B) Ge　(C) GaAs　(D) InAs

9. Predict the number of unpaired electron of the Mn spin-crossover complex [Mn(taa)] (H_3taa = tris(1-(2-azolyl)-2-azabuten-4-yl)amine) below its spin-crossover temperature. (A) 0　(B) 1　(C) 2　(D) 3

10. Predict the number of unpaired electrons for B_2, $[Cr(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{3+}$, respectively.
(A) 2, 0, 5　(B) 2, 2, 5　(C) 2, 0, 1　(D) 2, 4, 1

11. Predict the number of stereoisomers and pair of enantiomers for complex with formula, Ma_2b_2cd.
(M=metal; a, b, c, d = monodentate ligands), respectively. (A) 6, 2　(B) 7, 2　(C) 7, 3　(D) 8, 2

12. Predict the product distribution for the reaction of *fac*-$Mn(CO)_3(CH_3)(PMe_3)_2 + {}^{13}CO \rightarrow$



I　　II　　III　　IV

(A) 50%, 50%, 0%, 0%　(B) 25%, 25%, 25%, 25%　(C) 25%, 0%, 50%, 25%
(D) 25%, 25%,50%, 0%

13. Which one has the fastest water exchange rate?
(A) $[Cr(H_2O)_6]^{2+}$ (B) $[Mn(H_2O)_6]^{2+}$ (C) $[Fe(H_2O)_6]^{2+}$ (D) $[Co(H_2O)_6]^{2+}$

14. Choose the one that shows the strongest Jahn-Teller distortion.
(A) $[Ti(H_2O)_6]^{3+}$ (B) $[Cr(H_2O)_6]^{3+}$ (C) $[Mn(H_2O)_6]^{3+}$ (D) $[Co(H_2O)_6]^{3+}$

15. Decide the suitable first-row transition metal for $[\mathbf{M}(CO)_3(NO)]^-$ (NO: linear), which obeys the 18 e^- rule. (A) Cr (B) Mn (C) Fe (D) Co

16. What is the metal bond order for Ar'CrCrAr' [Ar' = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$]?
(A) 2 (B) 3 (C) 4 (D) 5

17. Decide the expected structure of $CPB_{10}H_{11}$. (A) *Hypho* (B) *Closo* (C) *Nido* (D) *Arachno*

18. Decide the isolobal fragments for I, Ni(η^5-C_5H_5) and II, (η^6-C_6H_6)Mn(PPh_3)$_2$, respectively.
(A) C, CH_2 (B) CH, CH_3 (C) CH_2, CH_2 (D) CH_3, CH_3

19. Methyl transfer reactions of cobalamines rely on the:
(A) low electrophilicity of square-planar Co(I) (B) high electrophilicity of square-planar Co(I)
(C) low nucleophilicity of square-planar Co(I) (D) high nucleophilicity of square-planar Co(I)

20. Which complex is importance in anti-cancer therapy?
(A) *cis*-$PtCl_2(NH_3)_2$ (B) $HCo(CO)_4$ (C) $RhCl(PPh_3)_3$ (D) *trans*-$Ir(CO)Cl(PEt_3)_2$

二、簡答題：(40 分)

1. Three isomers having the formula N_2CO are known:
I. ONCN (nitrosyl cyanide), II. ONNC (nitrosyl isocyanide), and III. NOCN (isonitrosyl cyanide).
(a) Draw the **most** important resonance structures of these isomers, and determine the formal charge for each atom. (9%)
(b) Which **isomer** do you predict to be the most stable (lowest energy) form? (1%)

2. (a) Use molecular orbital energy diagram of N_2 to explain that the first ionization energy of N_2 (1501 kJ/mol) is greater than the first ionization energy of atomic nitrogen (1402 kJ/mol). (5%)

(b) Describe the bonding scheme between a π-acceptor or a π-donor ligand and metal in a simplified MO diagram and also effects of π bonding on Δ (octahedral orbital splitting) (5%)

Ligand	F^-	NH_3	CN^-
Cr(III)Δ_{oct}(cm^{-1})	15200	17400	33500

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3. For SO_3:

(a) Obtain a reducible representation (Γ_{all}) based on ***all*** the motion of the atoms in SO_3. (2%)

(b) Calculate the number and symmetry of its **vibrational** modes. (4%)

(c) Which symmetry of vibrational modes are in the plane of the nuclei? (2%)

(d) Which symmetry of vibrational mode is perpendicular to the molecular plane? (2%)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

4. Arrange the increasing order for the following properties and give your explanation.

(a). Nephelauxetic effect for ligands of Cl^-, Br^- and I^-. (4%)

(b) The energy of ν_{CO} for $[V(CO)_6]^-$, $Cr(CO)_6$, and $[Mn(CO)_6]^+$. (3%)

(c). The energy of ligand to metal charge transfer band (LMCT) of CrO_4^{2-}, MoO_4^{2-}, and WO_4^{2-}. (3%)