

國立成功大學

112學年度碩士班招生考試試題

編 號：46

系 所：化學系

科 目：無機化學

日 期：0207

節 次：第 3 節

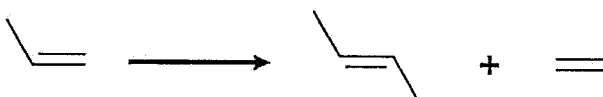
備 註：不可使用計算機

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

一、單選題：（50分，每題2.5分）

1. The Nobel Prize in Chemistry in 2022 was awarded to click chemistry, or the azide-alkyne cycloaddition to connect two molecular fragments. For their initial discovery, what metal ion was required as a catalyst for this reaction to proceed at a milder condition?

(A) Cu(I) (B) Zn(II) (C) Fe(II) (D) Fe(III) (E) Mo(II)

2. Name the following reaction: 

(A) Hydroformylation

(B) Sigma bond metathesis

(C) Hydrogenation

(D) Olefin metathesis

(E) Pauson-Khand reaction

3. Following Question 2, complexes based on what transition metals are used for this reaction as catalysts?

(A) Fe and Co (B) Pd and Pt (C) Ni and Zn (D) Cr and Mn (E) Mo and Ru

4. Spinel structures are based on cubic closed-packed arrangements of oxide ions. How many octahedral and tetrahedral holes are there in this unit cell, respectively?

(A) 1, 2 (B) 2, 4 (C) 3, 6 (D) 4, 8 (E) 5, 10

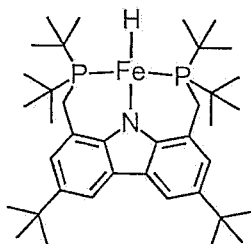
5. Following Question 4, if half of the octahedral holes and one-eighth of the tetrahedral holes are filled with Fe and Zn ions, respectively, what is the formula of the resulting oxide?

(A) Zn_2FeO_4 (B) $Zn_2Fe_2O_5$ (C) Zn_2FeO_3 (D) $ZnFe_2O_4$ (E) $ZnFeO_2$

6. What type of reaction is usually the last step in the Born-Haber cycle?

(A) Sublimation (B) Bond dissociation (C) Ionization (D) Lattice formation (E) Condensation

7. Below is a square planar Fe hydride complex that had the hydride resonance in the 1H NMR spectrum to be -3560 ppm, what is the oxidation state of Fe?

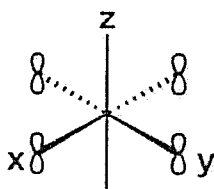


(A) 0 (B) +1 (C) +2 (D) +3 (E) +4

8. Following Question 7, what is the electron count of this complex?

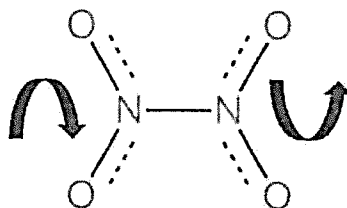
- (A) 14 (B) 16 (C) 18 (D) 19 (E) 20

9. What is the symmetry of the following ligand group orbital (LGO) in a D_{4h} point group?



- (A) A_{1g} (B) A_{2u} (C) E_u (D) A_{1u} (E) A_{2g}

10. What is the symmetry of the following vibration (i.e. torsion of two NO_2 planes)?

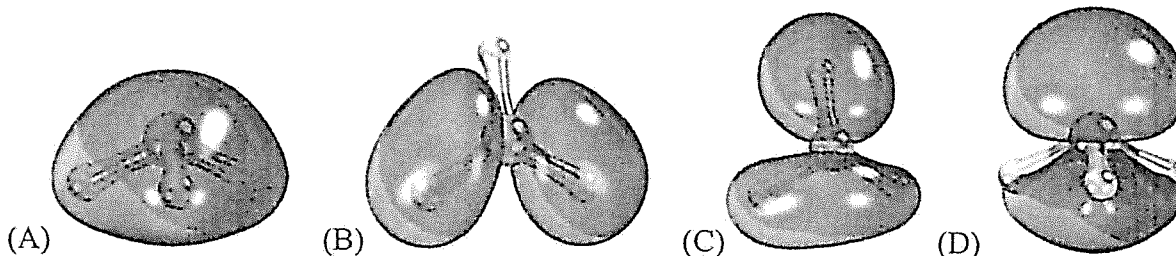


- (A) A_g (B) B_{1g} (C) B_{2g} (D) B_{3u} (E) A_u

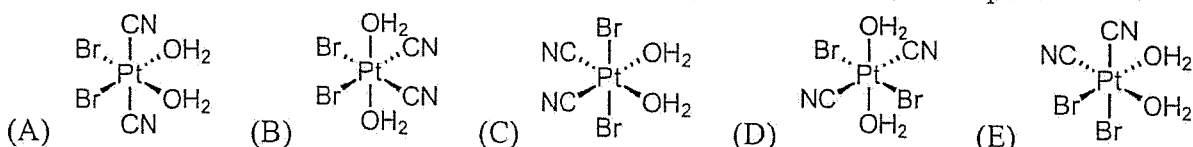
11. Following Question 10, is this vibration IR and Raman active/inactive?

- (A) IR and Raman active (B) IR and Raman inactive
 (C) IR active, Raman inactive (D) IR inactive, Raman active

12. Below are the bonding MOs of NH_3 . Which one is the HOMO (highest occupied molecular orbital)?

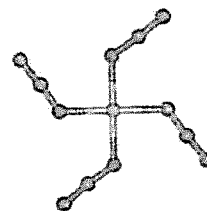


13. Below are the geometric isomers of $Pt(CN)_2Br_2(H_2O)_2$. Which one have an optical isomer?



14. Determine the point group of (square planar) tetraazidocopper(II).

- (A) C_{4v} (B) C_{4h} (C) D_{4h} (D) D_{4d} (E) C_4



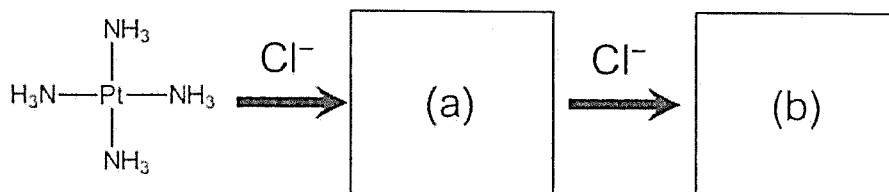
15. The magnetic moment of a green salt $K_n[VF_6]$ is $2.79 \mu_B$ (Bohr magneton number). What should be n ?

- (A) 1 (B) 2 (C) 3 (D) 4 (E) 5

16. Which one of the following metal complexes has the slowest water exchange rate?

- (A) $[V(H_2O)_6]^{3+}$ (B) $[Ir(H_2O)_6]^{3+}$ (C) $[Na(H_2O)_6]^+$ (D) $[Ca(H_2O)_6]^{2+}$ (E) $[Mn(H_2O)_6]^{3+}$

17. What would be the major product of (b)? Note: the charge of the complex ions is not shown. The oxidation states of Pt are all +2.



- (A) $\begin{array}{c} \text{NH}_3 \\ | \\ \text{Cl}-\text{Pt}-\text{NH}_3 \\ | \\ \text{NH}_3 \end{array}$ (B) $\begin{array}{c} \text{NH}_3 \\ | \\ \text{Cl}-\text{Pt}-\text{Cl} \\ | \\ \text{NH}_3 \end{array}$ (C) $\begin{array}{c} \text{Cl} \\ | \\ \text{Cl}-\text{Pt}-\text{Cl} \\ | \\ \text{NH}_3 \end{array}$ (D) $\begin{array}{c} \text{Cl} \\ | \\ \text{Cl}-\text{Pt}-\text{NH}_3 \\ | \\ \text{NH}_3 \end{array}$ (E) $\begin{array}{c} \text{Cl} \\ | \\ \text{Cl}-\text{Pt}-\text{Cl} \\ | \\ \text{Cl} \end{array}$

18. How many unpaired electrons are found in $[Dy(H_2O)_6]^{3+}$?

- (A) 3 (B) 4 (C) 5 (D) 6 (E) 7

19. Determine the ground state free-ion term symbol ($^{2S+1}L_J$) of Dy^{3+} .

- (A) $^6H_{15/2}$ (B) $^8S_{7/2}$ (C) 5I_4 (D) 3H_4 (E) $^6H_{5/2}$

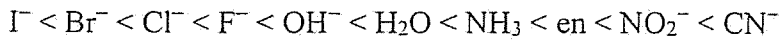
20. Rank the following complex ions in order of increasing wavelength of light absorbed: $[Co(H_2O)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[CoI_6]^{3-}$, and $[Co(en)_3]^{3+}$

- (A) $[Co(CN)_6]^{3-} < [Co(en)_3]^{3+} < [Co(H_2O)_6]^{3+} < [CoI_6]^{3-}$
 (B) $[Co(CN)_6]^{3-} < [CoI_6]^{3-} < [Co(en)_3]^{3+} < [Co(H_2O)_6]^{3+}$
 (C) $[CoI_6]^{3-} < [Co(en)_3]^{3+} < [Co(H_2O)_6]^{3+} < [Co(CN)_6]^{3-}$
 (D) $[Co(CN)_6]^{3-} < [Co(H_2O)_6]^{3+} < [Co(en)_3]^{3+} < [CoI_6]^{3-}$
 (E) $[CoI_6]^{3-} < [Co(H_2O)_6]^{3+} < [Co(en)_3]^{3+} < [Co(CN)_6]^{3-}$

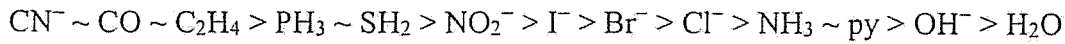
二、問答題：(50分)

21. Let's consider cubic unit cells: (10%)
- How many spheres (or atoms) in total does a body-centered cubic unit cell have? Draw the unit cell and show your work. (5%)
 - Draw a simple cubic unit cell. Calculate the packing efficiency of a simple cubic unit cell. (5%)
22. Let's consider a hypothetical square planar transition metal complex $\text{Pd}(\text{CH}_3)_4$. (15%)
- Draw a qualitative molecular orbital diagram for the complex $\text{Pd}(\text{CH}_3)_4$. Provide an appropriate symmetry label for each molecular orbital, and fill in the electrons. (7%)
 - Draw a qualitative d-orbital splitting diagram for $\text{Pd}(\text{CH}_3)_4$ using a crystal field theory approach. Remember to label d-orbitals. (6%)
 - Do your answers of the d-orbital splitting to parts (a) and (b) agree? Briefly explain why or why not. (2%)
23. Sketch the structure of the following transition metal complexes as accurately as possible and clearly show the electron counting. Show your work in electron counting. You can use either covalent or ionic method. (9%)
- $\text{Zr}(\text{CH}_3)_6^{2-}$ (3%)
 - $\text{Fe}(\text{CO})_5$ (3%)
 - $\text{Mn}(\text{CH}_3)_4\{\text{P}(\text{CH}_3)_3\}_2$ (3%)
24. Explain why $[\text{MnF}_6]^{3-}$ has Jahn-Teller distortion, but $[\text{Mn}(\text{CN})_6]^{3-}$ does not. Calculate $\mu_{\text{spin-only}}$ for both complexes. (10%)
25. The compound cisplatin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, has been studied extensively as an antitumor agent. The reaction for the synthesis of cisplatin is:
- $$\text{K}_2\text{PtCl}_4(\text{aq}) + 2 \text{NH}_3(\text{aq}) \rightarrow \text{Pt}(\text{NH}_3)_2\text{Cl}_2(\text{s}) + 2 \text{KCl}(\text{aq})$$
- Write the electron configuration for platinum ion in cisplatin. Most d^8 transition metal ions exhibit square planar geometry. Draw the structure of cisplatin and give chemical names for cisplatin based on either Stock system or Ewing-Bassett system. (6%)

Spectrochemical series:



Trans effect for Pt(II) complexes:



$\mu_{spin-only} = \sqrt{4S(S+1)} = \sqrt{n(n+2)}$

Character Table

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	$h = 8$
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

D_{4h}	E	$2C_4(z)$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	$h = 16$
A_{1g}	1	1	1	1	1	1	1	1	1	1	x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y) (xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57/71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89/103	104 Rf (267)	105 Db (268)	106 Sg (271)	107 Bh (272)	108 Hs (270)	109 Mt (276)	110 Ds (291)	111 Rg (280)	112 Cn (285)	113 Nh (284)	114 Fl (289)	115 Mc (288)	116 Lv (293)	117 Ts (294)	118 Og (294)

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.2	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac (227)	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (251)	98 Cf (252)	99 Es (257)	100 Fm (258)	101 Md (259)	102 No (262)	103 Lr (262)