國立成功大學

114學年度碩士班招生考試試題

編　號：43

系　所：化學系

科　目：無機化學

日　期：0211

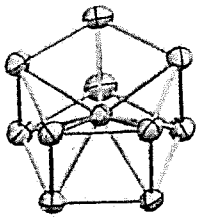
節　次：第 3 節

注　意：1.不可使用計算機
2.請於答案卷(卡)作答，於試題上作答，不予計分。

一、單選題：（50 分，每題 2.5 分）

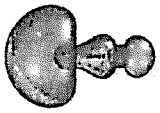
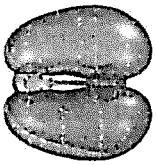
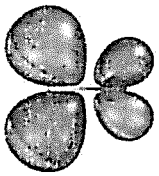
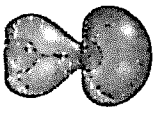
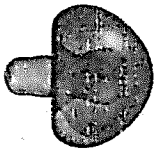
1. Which of the following is not considered a fundamental symmetry operation in molecular geometry?
(A) improper rotation (B) proper rotation (C) reflection (D) glide reflection (E) inversion

2. Determine the point group of the following cluster anion $[Fe@Ge_{10}]^{3-}$.



(A) D_{5h} (B) D_{5d} (C) C_{5h} (D) C_{5v} (E) O_h

3. Which one of the following is the highest occupied molecular orbital for the CO molecule? Note: for clarity, the atom on the left is carbon, and the atom on the right is oxygen.

(A)  (B)  (C)  (D)  (E) 

4. Which of the following ions is classified as hard acid?
(A) F^- (B) Br^- (C) Na^+ (D) Cs^+ (E) S^{2-}

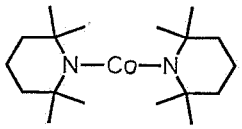
5. Which of the following is a d^2 ion?
(A) Mn^{3+} (B) Ti^+ (C) Fe^{3+} (D) Cr^{2+} (E) Ti^{2+}

6. How many microstates are there for a d^2 free ion?
(A) 2 (B) 5 (C) 25 (D) 45 (E) 80

7. Following Question 6, according to Hund's rule, what is the lowest energy atomic state?
(A) ^1G (B) ^3F (C) ^1D (D) ^3P (E) ^1S

8. Which of the following statements about the complex ion $[Co(en)_2Cl_2]^+$ is correct? (en = ethylenediamine)
(A) It has two geometric isomers and two optical isomers.
(B) Since en is a strong field ligand, the complex ion is paramagnetic.
(C) It has *cis* and *trans* geometric isomers, but no optical isomers.
(D) The geometric isomers of it have similar properties.
(E) The oxidation state of Co is +1.

9. Below is a new coordination complex reported in 2024, what is the electron count of the metal center?



(A) 9 (B) 10 (C) 11 (D) 12 (E) 13

10. Following Question 9, what is the possible spin state (*S*) of the complex?

(A) $^1/_2$ and $^3/_2$ (B) 0 and 1 (C) 1 and $^3/_2$ (D) $^1/_2$ and $^5/_2$ (E) 1 and 2

11. In a transition metal complex having O_h symmetry, which configurations in the following can be classified as *E*?

(A) $t_{2g}^5e_g^2$ (B) $t_{2g}^3e_g^3$ (C) $t_{2g}^5e_g^0$ (D) $t_{2g}^4e_g^2$ (E) $t_{2g}^3e_g^0$

12. Arrange the acidity in water for (A) $HCo(CO)_4$, (B) $HCo(CO)_3\{P(OPh)_3\}$, and (C) $HCo(CO)_3(PPh_3)$.

(A) A > B > C (B) A > C > B (C) B > C > A (D) C > B > A (E) B > A > C

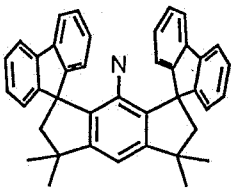
13. Arrange the acidity in acetonitrile for (A) $H_2Fe(CO)_4$, (B) $H_2Ru(CO)_4$, and (C) $H_2Os(CO)_4$.

(A) A > B > C (B) A > C > B (C) B > C > A (D) C > B > A (E) B > A > C

14. Predict the number of radial nodes and angular nodes for a 4d orbital.

(A) 3, 1 (B) 2, 1 (C) 1, 2 (D) 0, 3 (E) 1, 3

15. The following is a stable nitrene molecule isolated by Beckmann and coworkers in 2024. What is the oxidation state of N?



(A) +1 (B) −1 (C) +2 (D) −3 (E) +3

16. Which of the following molecules is paramagnetic?

(A) N_2 (B) B_2 (C) He_2 (D) C_2 (E) F_2

17. An element crystallizes in a face-centered cubic structure. What is the relationship between the radius of that atom (*r*) and the length of an edge of the unit cell (*l*)?

(A) $r = 2l$ (B) $r = \frac{l}{\sqrt{8}}$ (C) $r = \sqrt{8}l$ (D) $r = \frac{\sqrt{3}}{4}l$ (E) $r = \frac{l}{2}$

18. The triple point of CO_2 is at 5.2 atm and −57 °C. Under a typical atmospheric condition in Yushan (P = 481 torr, T = 3.8 °C), a sample of dry ice (solid CO_2) will
(A) melt (B) boil (C) sublime (D) remain solid (E) none of the above

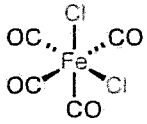
19. Rank in order of increasing energy for the following spectroscopic techniques in inorganic chemistry: A. NMR spectroscopy B. EPR spectroscopy C. Electronic spectroscopy D. Vibrational spectroscopy E. Extended X-ray absorption fine structure
(A) ABCDE (B) EDCBA (C) ABDCE (D) ECABD (E) BACDE

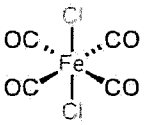
20. What is the multiplicity of the ^{31}P NMR signal in the octahedral PF_6^- anion in solution? (^{31}P, $I = {}^1/_2$; ^{19}F, $I = {}^1/_2$)
(A) singlet (B) doublet (C) quartet (D) sextet (E) septet

二、問答題：（50 分）

21. (13 points) Consider the NO molecule:
(A) (3 points) Draw the most stable Lewis structure of this molecule. What are the oxidation states and formal charges of each element?
(B) (5 points) Construct the molecular orbital diagram of NO. Use the following orbital potential energies to construct the MO diagram: N 2s: −25.56 eV, 2p: −13.18 eV. O 2s: −32.38 eV, 2p: −15.85 eV.
(C) (2 points) Predict the bond order and the number of unpaired electrons of NO from your results of (A) and (B).
(D) (3 points) Both NO^+ and NO^- are well-known in inorganic chemistry. Based on the molecular orbital diagram results in (B), what are the bond orders of these two ions? Which one of these three would have the shortest N−O bond distance? Briefly explain.

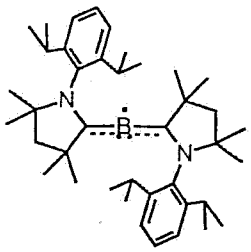
22. (9 points) $Fe(CO)_4Cl_2$ has two isomers (A) and (B), determine the number of IR- and Raman-active C−O stretching vibrations for both. Is IR or Raman spectroscopy able to distinguish them? Show your work clearly to receive points.

(A) 

(B) 

23. (12 points, 4 points each) Using the angular overlap model, draw the d-orbital energy splitting diagrams and determine the energy differences between the d orbitals of the metal for the following geometries for monodentate σ-donor (L) ligands.
(A) Octahedral ML_6 complex.
(B) Trigonal planar ML_3 complex.
(C) Square pyramidal ML_5 complex.

24. (6 points) The following molecule is a monoatomic B(0) molecule reported in 2024 by Pranckevicius and coworkers. The authors draw the following Lewis structure that has a partial double bond between boron and carbon and a radical on boron. List at least three experimental techniques that could be used to support their proposed structure and briefly explain your reasoning.



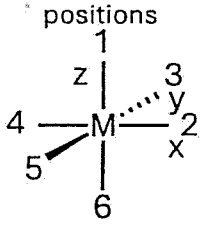
25. (10 points) The salt LiBr has a Li–Br distance of 275 pm (1 pm = 10^{-12} m) and has the NaCl structure.
    (A) (3 points) Draw the unit cell of the molecule.
    (B) (2 points) How many atoms of Li and Br are there in a unit cell?
    (C) (2 points) Calculate the mass of a unit cell.
    (D) (3 points) What is the density of LiBr?

Spectrochemical series: $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < en < NO_2^- < CN^-$

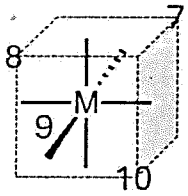
$\mu_{spin\text{-}only} = \sqrt{4S(S+1)} = \sqrt{n(n+2)}$

Angular Overlap Method (AOM) for Metal ligand σ-interactions

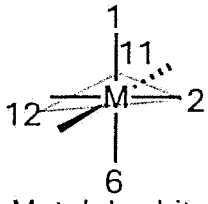
Octahedral positions



Tetrahedral positions



Trigonal bipyramidal positions



σ-interactions (in terms of e_σ) for Metal d-orbitals

Ligand Position	z^2	x^2-y^2	xy	xz	yz
1	1	0	0	0	0
2	$^1/_4$	$^3/_4$	0	0	0
3	$^1/_4$	$^3/_4$	0	0	0
4	$^1/_4$	$^3/_4$	0	0	0
5	$^1/_4$	$^3/_4$	0	0	0
6	1	0	0	0	0
7	0	0	$^1/_3$	$^1/_3$	$^1/_3$
8	0	0	$^1/_3$	$^1/_3$	$^1/_3$
9	0	0	$^1/_3$	$^1/_3$	$^1/_3$
10	0	0	$^1/_3$	$^1/_3$	$^1/_3$
11	$^1/_4$	$^3/_{16}$	$^9/_{16}$	0	0
12	$^1/_4$	$^3/_{16}$	$^9/_{16}$	0	0

Character Table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

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 (281)	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 (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)