國立成功大學
111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：0220

節　次：第 3 節

備　註：不可使用計算機

編號： 46

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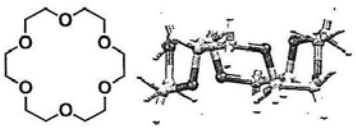
※考生請注意：本試題不可使用計算機。請於答案卷（卡）作答，於本試題紙上作答者，不予計分。

一、單選題：（50 分，每題 2.5 分）

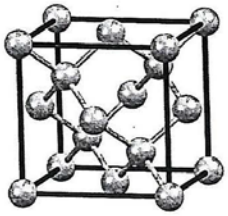
1. Determine the point group of a d_{xy} orbital.
   (A) C_{2v} (B) D_{2h} (C) C_{2h} (D) T_d (E) O_h

2. Determine the point group of 18-crown-6 in the solid state. The drawing (top-view) and the ball-and-stick model (side-view) are shown below for your reference:



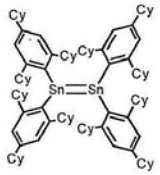
   (A) C_{6v} (B) C_{6h} (C) D_{6d} (D) D_{6h} (E) S_6

3. The unit cell of Si is shown below. How many Si atoms can be found in the unit cell?



   (A) 3 (B) 4 (C) 6 (D) 8 (E) 12

4. Below is a recently reported solution-stable distannene, a heavier analogue of alkene (Cy = cyclohexyl, C_6H_{11}). What is the oxidation state of Sn?



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

5. Following Question 4, what is the electron count of Sn?
   (A) 4 (B) 6 (C) 8 (D) 10 (E) 18

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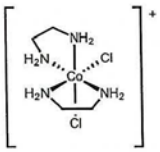
6. Polar molecules have a non-zero net dipole moment. Therefore, for a molecule to be polar, what symmetry element(s) must it not have?
   A. i; B. σ_h; C. σ_v; D. a principal C_n axis; E. perpendicular C_2 axes
   (A) A, B, E　(B) A, B　(C) A, B, C, D, E　(D) D, E　(E) C, D, E

7. For the following point groups, which one(s) can be chiral?
   A. D_{5d}; B. D_4; C. C_2; D. S_6; E. C_1; F. T_d
   (A) B, C, E　(B) A, B, C, D, E　(C) A, B, C, D, E, F　(D) B, C, D, E　(E) A, C, E

8. Name the following coordination complex:



   (A) Δ-*fac*-dichlorobis(ethylenediamine)cobalt(III)
   (B) Δ-*cis*-dichlorobis(ethylenediamine)cobalt(II)
   (C) Λ-*cis*-dichlorobis(ethylenediamine)cobalt(III)
   (D) Λ-*trans*-dichlorobis(ethylenediamine)cobalt(II)
   (E) Δ-*cis*-dichlorobis(ethylenediamine)cobalt(III)

9. Based on the 18-electron rule, identify the first-row transition metal for $M(CO)_7^+$.
   (A) Ti　(B) V　(C) Cr　(D) Mn　(E) Fe

10. Predict the number of IR-active C−O stretching band(s) for $Cr(CO)_3(\eta^6\text{-}C_6H_6)$ assuming C_{3v} point group.
    (A) 5　(B) 4　(C) 3　(D) 2　(E) 1

11. High-spin Mn(II) complexes, regardless of their coordination geometry and ligand environment, usually have very faint colors (pale yellow or pink). Pick the correct reasoning.
    (A) Manganese is not a transition metal.
    (B) All of their d orbitals are half-filled, making the electronic transition spin-forbidden.
    (C) All of their d orbitals are filled, therefore, there is no electronic transition in the visible light region.
    (D) The electronic transition is in the UV region.
    (E) The ground state of these complexes is singlet.

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12. Predict the spin-only magnetic moment ($\mu_{spin\text{-}only}$, in Bohr magneton number) of $FeCl_4^-$.
(A) 1.73 (B) 2.83 (C) 3.87 (D) 4.90 (E) 5.92

13. The crystalline Mg has the following unit cell parameters: a = b = 3.203 Å, c = 5.127 Å, α = β = 90°, γ = 120°, What is its crystal system?
(A) monoclinic (B) triclinic (C) rhombohedral (D) tetragonal (E) hexagonal

14. How many molecular orbitals would a water (H_2O) molecule have (consider only its valence orbitals)?
(A) 4 (B) 5 (C) 6 (D) 7 (E) 8

15. Which of the following complexes will absorb visible light radiation of the shortest wavelength?
(A) $Co(OH)_6^{3-}$ (B) CoI_6^{3-} (C) $Co(H_2O)_6^{3+}$ (D) $Co(en)_3^{3+}$ (E) $Co(NH_3)_6^{3+}$

16. In which of the following complexes does the transition metal have a d^8 electron configuration?
(A) $Ti(H_2O)_6^{2+}$ (B) $Ni(CO)_4$ (C) $Mn(CN)_6^{3-}$ (D) $NiCl_4^{2-}$ (E) $Zn(NH_3)_4^{2+}$

17. Which one of the following crown ethers are most suited for Li^+?
(A) 12-crown-4 (B) 15-crown-5 (C) 18-crown-6 (D) 21-crown-7 (E) 24-crown-8

18. Gas phase proton affinity is a method to directly compare the Brønsted-Lowry base strength without the solvent effect. Pick the correct Brønsted-Lowry base strength ranking in gas phase:
(A) $NMe_3 > NHMe_2 > NH_2Me > NH_3$
(B) $NH_3 > NH_2Me > NHMe_2 > NMe_3$
(C) $NHMe_2 > NMe_3 > NH_2Me > NH_3$
(D) $NH_3 > NMe_3 > NHMe_2 > NH_2Me$
(E) $NMe_3 > NH_2Me > NHMe_2 > NH_3$

19. What is the point group of the character table?

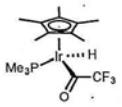
	E	$2C_4$	$C_2(z)$	$2C'_2$	$2C''_2$
A	1	1	1	1	1
B	1	1	1	−1	−1
C	1	−1	1	1	−1
D	1	−1	1	−1	z
E	x	0	y	0	0

(A) C_{4h} (B) D_{4h} (C) D_{4d} (D) C_4 (E) D_4

20. Following Question 19, which statement is incorrect?
(A) The order of the point group is 8.
(B) There are 5 classes of symmetry elements.
(C) The Mulliken symbol of A is A_1.
(D) The Mulliken symbol of C is B_2.
(E) $x + y + z = 1$.

二、問答題：（50 分）

21. Cordaro and Bergman have reported the following iridium complex, what spectroscopic methods could be used to identify it? List 3 of them and give an indication of the expected spectroscopic features. (3 each, 9% total)



22. Read the paragraph and answer the following questions accordingly: (16%)

Boron monofluoride (BF) and carbon monoxide (CO) are isoelectronic with 10 valence electrons. While CO is readily available and is a common ligand to almost all transition metals, BF is unstable at room temperature, making its coordination chemistry limited. Here, Figueroa, Neidig, and coworkers reported the isolation of the first Fe complex with BF as the terminal ligand. The complex had the molecular formula of $Fe(BF)(CO)_2(CNAr)_2$, where Ar is a bulky aryl substituent. For comparison, they also synthesized analogous complexes with the isoelectronic dinitrogen (N_2) and CO ligands, $Fe(N_2)(CO)_2(CNAr)_2$ and $Fe(CO)_3(CNAr)_2$. These complexes were characterized by single-crystal x-ray diffraction, nuclear magnetic resonance, infrared, and Mössbauer spectroscopies. These studies concluded that the terminal BF ligand had strong σ-donating and π-accepting properties compared to the isoelectronic CO and N_2 ligands.

(a) Draw the most stable Lewis structures of BF, CO, and N_2. (6%)
(b) Draw the molecular structure of $Fe(BF)(CO)_2(CNAr)_2$, use "Ar" to denote the isocyanide substituent, what might be the most stable geometry about the metal center? (4%)
(c) The authors used several techniques to characterize their complexes, list 3 of them and briefly (in 1 sentence) describe the information that can be obtained from these techniques. (6%)

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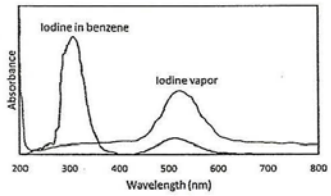
23. Sketch a *neutral 18-electron structure* for the following metals and ligands. **Use at least one metal and each type of ligand shown.** Keep your structure as simple as possible (use only 1 metal center). Clearly show your electron counting and indicate the metal oxidation state. Draw a reasonable structure showing the geometry about the metal center(s). (5% each, 10%)
    (a) Pt, CH_3^-, PPh_3, H^-.
    (b) Re, η^5-Cp^- (cyclopentadienyl), C≡NMe.

24. Explain the change of electronic absorption transition of I_2 in gas phase (I_2 vapor) and I_2 dissolved in benzene. Hint: Use simple MO diagram to explain. I_2 is a Lewis acid and benzene is a Lewis base. (7%)



25. Lithium oxide adopts the cubic antifluorite structure when crystallized. In the unit cell, the oxide anions have cubic close packing (CCP) and the lithium cations occupy all the tetrahedral holes. Based on the information, draw the unit cell of lithium oxide, and determine the number of lithium cations and oxide anions in the unit cell. (8%)

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Useful Information

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

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

Character Table

C_{3v}	E	$2C_3$	$3\sigma_v$	linear	quadratic
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

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)