編號： 50

國立成功大學 109 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：0211，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、單選題：（40 分，每題 2 分）

1. Rank in order of increasing energy for the following spectroscopic techniques for inorganic chemistry: A. EPR spectroscopy B. Mößbauer spectroscopy C. Infrared spectroscopy D. UV-Vis (electronic) spectroscopy E. X-ray absorption spectroscopy (XAS)
   (A) A < B < C < D < E (B) A < C < D < E < B (C) E < D < C < B < A (D) C < A < D < B < E

2. Determine the point group of triflate ion, $F_3CSO_3^-$.
   (A) C_{3h} (B) C_{2v} (C) D_{3d} (D) C_{3v} (E) D_{3h}

3. Determine the point group of $Os_2Cl_8^{2-}$ (staggered).
   (A) D_{4h} (B) D_{4d} (C) C_{4h} (D) C_{4v} (E) D_4

4. Which metal hydride, in each of the following pairs of compounds, should be more acidic?
   (a) $HV(CO)_6$ or (b) $HV(CO)_3(PPh_3)_3$
   (c) $HRh(CO)(PPh_3)_2$ or (d) $HRh(CO)_2\{P(OPh)_3\}$
   (A) (a) and (c) (B) (a) and (d) (C) (b) and (c) (D) (b) and (d)

5. For the compound that contains only one Fe environment, which Mößbauer spectrum would you NOT expect?
   (A) a singlet (B) a doublet (C) a triplet (D) a sextet

6. Which of the following acids is the strongest?
   (A) $Fe(H_2O)_6^{3+}$ (B) $Fe(H_2O)_6^{2+}$ (C) $Co(H_2O)_6^{2+}$ (D) $Ni(H_2O)_6^{2+}$ (E) $Zn(H_2O)_6^{2+}$

7. Pick the INCORRECT statement about early transition metals.
   (A) They are oxophilic.
   (B) They prefer lower oxidation states.
   (C) They are more electropositive than late transition metals.
   (D) Some of them are useful catalysts in olefin polymerization.
   (E) They are usually classified as hard metals.

8. Determine the electron count for U in $U(cot)_2$ (cot = cyclooctatetraenyl dianion).
   (A) 18 (B) 22 (C) 24 (D) 28 (E) 32

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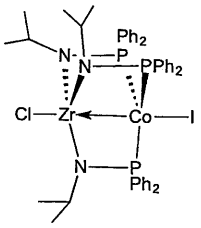
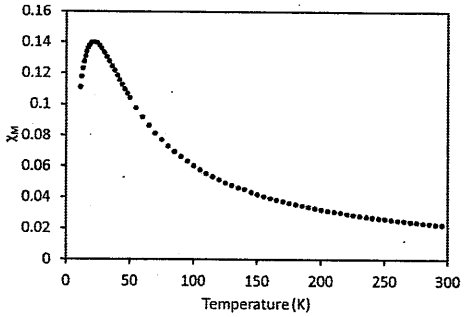
9. Determine the electron count for Zr and Co in the following complex, respectively.



(A) 10, 16　(B) 10, 18　(C) 18, 18　(D) 10, 10　(E) 16, 10

10. What type of compounds or materials might exhibit the following behavior?

(A) paramagnetic　(B) superparamagnetic　(C) ferromagnetic　(D) antiferromagnetic



11. What is NOT the typical behavior of a single molecule magnet (SMM)?

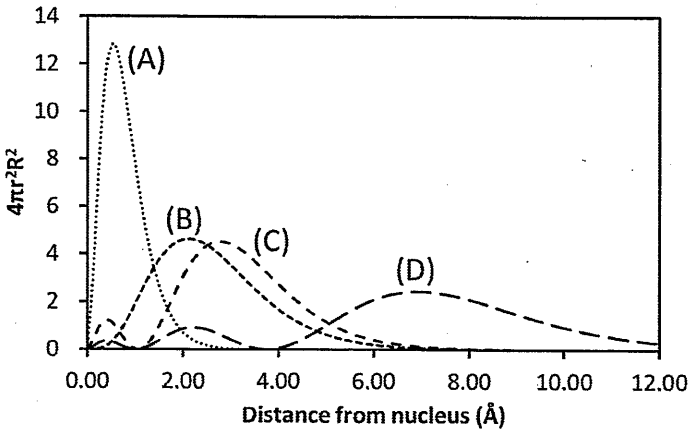
(A) slow magnetization relaxation　(B) magnetic hysteresis

(C) long range ordering　(D) typically consist of high-spin metal ions

12. What is the LUMO of O_2?

(A) σ_u　(B) π_g　(C) σ_g　(D) π_u　(E) δ_g

13. Below is the radial probability plot of the H atom, which one is most likely to be the 2p orbital?

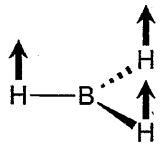


14. A crystal has the following cell parameters, what is the crystal system?
$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$
(A) cubic (B) orthorhombic (C) triclinic (D) monoclinic (E) tetragonal

15. Which one of the following complexes has an effective magnetic moment (μ_{eff}) close to 5.9?
(A) $Fe(CN)_6^{4-}$ (B) $Mn(H_2O)_6^{2+}$ (C) $Cu(H_2O)_6^{2+}$ (D) $Ni(H_2O)_6^{2+}$ (E) $Co(H_2O)_6^{3+}$

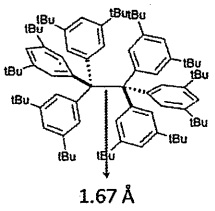
16. What is NOT a vibration normal mode of ethylene?
(A) a_g (B) b_{2g} (C) a_u (D) b_{3u} (E) b_{3g}

17. What is the following symmetry type of the vibration normal mode?



(A) e' (B) a_1' (C) e" (D) a_1'' (E) a_2'

18. The following compound has an unusually long C–C bond length of 1.67 Å in the solid state, what is the main contributing force to the stability of this compound?



(A) hydrogen bond (B) dipole-dipole (C) dipole-induced dipole (D) dispersion (E) ionic bond

19. One of the E_g SALCs for the octahedral complex is

$$\Psi_{e_g}^1 = \frac{1}{2}(L_3 - L_4 + L_5 - L_6)$$

What could be the other one?

(A) $\frac{1}{\sqrt{12}}(2L_1 + 2L_2 - L_3 - L_4 - L_5 - L_6)$ (B) $\frac{1}{\sqrt{6}}(L_1 + L_2 - L_3 - L_4 - L_5 - L_6)$

(C) $\frac{1}{\sqrt{6}}(L_1 + L_2 + L_3 + L_4 + L_5 + L_6)$ (D) $\frac{1}{\sqrt{18}}(-L_1 - L_2 + 2L_3 + 2L_4 + 2L_5 + 2L_6)$

(E) $\frac{1}{\sqrt{12}}(2L_1 + 2L_2 + L_3 + L_4 + L_5 + L_6)$

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20. What is the Mo–Mo bond order for $Mo_2(CH_2Ph)_6$?
    (A) 1　(B) 2　(C) 3　(D) 4　(E) 5

二、問答題：（60 分）

21. Consider the octahedral vanadyl ion, $VO(H_2O)_5^{2+}$: (15%)
    (a) First, construct the molecular orbital diagram of square pyramidal $V(H_2O)_5^{4+}$. Assume that H_2O is a pure σ donor. Provide an appropriate label for each molecular orbital, sketch each molecular orbital, and fill in the correct number of electrons. (6%)
    (b) Use the MO you created in (a), construct the MO diagram of octahedral $VO(H_2O)_5^{2+}$ with $V(H_2O)_5^{4+}$ and O^{2-} ion. For simplicity, you can use the 3d orbitals for V. Provide an appropriate label for each molecular orbital, sketch each molecular orbital, and fill in the correct number of electrons. (7%)
    (c) Based on your MO, what is the bond order between V and the O^{2-} ligand? (2%)

22. Consider the molecule, $Pd(PPh_3)_3$, which has a maximum point group symmetry of D_{3h}: (15%)
    (a) Write down the symmetry labels for each of the Pd s, p, and d orbitals in the D_{3h} point group. (2%)
    (b) Draw each SALC and give it a symmetry label. Assume that PPh_3 is a pure σ donor. Provide an appropriate label for each molecular orbital, sketch each molecular orbital, and fill in the correct number of electrons. (4%)
    (c) Draw an MO diagram for $Pd(PPh_3)_3$. (6%)
    (d) What is the bond order for $Pd(PPh_3)_3$? (2%)
    (e) Is $Pd(PPh_3)_3$ paramagnetic or diamagnetic? (1%)

23. The complex, $K[Cu(CF_3)_4]$, contains a square planar Cu complex. (10%)
    (a) Assign the formal oxidation state of Cu in this species. (2%)
    (b) Experiment and computation showed that this species has a $4s^03d^{10}$ electronic configuration. Account for this observation by means of a simplified MO approach. (8%)

24. What is Tolman cone angle? Explain how it can influence the following equilibrium. How may this be important to catalysis? (10%)

$$Ni(PR_3)_4 \rightleftharpoons Ni(PR_3)_3 + PR_3$$

25. Why is X-ray crystallography not useful for the characterization of transition metal dihydrogen complex? Name at least two other methods that are useful and briefly elaborate. (10%)

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Character tables

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	+1	+1	+1	+1	+1	z	x^2+y^2, z^2
A_2	+1	+1	+1	−1	−1	R_z	
B_1	+1	−1	+1	+1	−1		x^2-y^2
B_2	+1	−1	+1	−1	+1		xy
E	+2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

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)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
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	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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)	