國立成功大學

110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：0203

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（卡）作答，於本試題紙上作答者，不予計分。
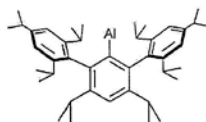
一、單選題：（40分，每題2分）

1. What is the ground state term symbol of Pr^{3+}?
   (A) $^3H_4$　(B) $^4I_{9/2}$　(C) $^7F_0$　(D) $^1S_0$　(E) $^5L_4$

2. Following Question 1, the effective magnetic moment (μ_{eff}) of lanthanide ions could be calculated using the following formula

   $$\mu_{eff} = g_J\sqrt{J(J+1)}, \text{ where } g_J = \frac{3}{2} + \frac{S(S+1)-L(L+1)}{2J(J+1)}$$
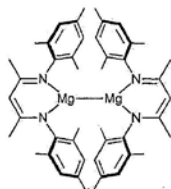
   where S and L are the total spin and orbital angular momentum, respectively. J is the total angular momentum. Use the above information, calculate μ_{eff} for Pr^{3+} ion.
   (A) 10.65　(B) 2.68　(C) 9.72　(D) 7.94　(E) 3.58

3. The molecule below is a recently reported compound containing a one-coordinate Al. What is the oxidation state of Al?
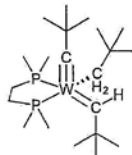

   (A) 0　(B) +1　(C) +2　(D) +3　(E) +4

4. Following Question 3, what is the electron count of Al?
   (A) 2　(B) 4　(C) 6　(D) 8　(E) 18

5. Determine the point group of mer-$[OsCl_3(CO)_3]^-$.
   (A) C_{3h}　(B) C_{2v}　(C) D_{3d}　(D) C_{3v}　(E) D_{3h}

6. Determine the point group of BrF_5.
   (A) D_{5h}　(B) D_{4d}　(C) C_{4h}　(D) C_{4v}　(E) C_{5v}

7. How many CO stretching bands could be observed in $Fe(CO)_5$?
   (A) 1　(B) 2　(C) 3　(D) 4　(E) 5

8. Based on Pearson's HSAB principle, which one of the following bases forms most favorably with Zn^{2+} ion?
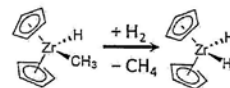   (A) F^-　(B) Cl^-　(C) Br^-　(D) I^-

9. Determine the valence (number of electrons an atom used in bonding) and oxidation state of Mg of the following compound.

(A) 1 and +1　　(B) 1 and +2　　(C) 2 and +1　　(D) 2 and +2　　(E) 3 and +1

10. The tetrahedral complex, Fe(cyclohexyl)$_4$, is diamagnetic. Pick the incorrect statement.
   (A) The oxidation state of Fe is +4.
   (B) It is a high-spin complex.
   (C) Cyclohexyl is a strong field ligand.
   (D) It can be regarded as an organometallic complex.
   (E) The ground state is singlet.

11. Determine the electron count for Ru in $[Ru(\eta^6\text{-}C_6H_6)_2]^{2+}$ (C_6H_6 = benzene).
   (A) 18　 (B) 16　 (C) 14　 (D) 20　 (E) 22

12. Determine the electron count for W in the following complex.

   (A) 12　 (B) 14　 (C) 16　 (D) 18　 (E) 20

13. For the following reaction, what could be the most probable mechanism?

   (A) σ-bond metathesis　　　　　　　　(B) migratory insertion
   (C) β-hydrogen elimination　　　　　　(D) oxidative addition and reductive elimination

14. Which one of the following reactions is spontaneous?
   (A) $Fe^{3+} + e^- \rightarrow Fe^{2+}$　 (B) $Cu^+ + e^- \rightarrow Cu$　 (C) $V^{3+} + e^- \rightarrow V^{2+}$
   (D) $Sc^{3+} + 3e^- \rightarrow Sc$　　 (E) $Al^{3+} + e^- \rightarrow Al^{2+}$

15. What is the symmetry of the vibration?

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

16. Which of the following complexes is not chiral? (en = ethylenediamine, acac = acetylacetonate, ox = oxalate)

    (A) *trans*-$[Co(en)_2Cl_2]^+$ (B) *cis*-$[Co(en)_2Cl_2]^+$ (C) $Fe(acac)_3$ (D) $[Zn(en)_3]^{2+}$ (E) $[Ti(ox)_3]^{2-}$

17. Which one of the following ligands is not a good π-acceptor?

    (A) NO　　(B) CO　　(C) NMe_3　　(D) $H_2C=CH_2$　　(E) N_2

18. The following reactions are typical in inorganic chemistry. Which one is metathesis?

    (A) $SO_3 + (CH_3)_2O \rightarrow O_3S-O(CH_3)_2$

    (B) $(CH_3CH_2)_2O-BF_3 + C_5H_5N \rightarrow C_5H_5N-BF_3 + (CH_3CH_2)_2O$

    (C) $Ni^{2+} + 6\ NH_3 \rightarrow Ni(NH_3)_6^{2+}$

    (D) $Me_3SiI + AgBr \rightarrow Me_3SiBr + AgI$

19. What is the Tc−Tc bond order in $K_3(Tc_2Cl_8)$?

    (A) 3　　(B) 3.5　　(C) 4　　(D) 4.5　　(E) 5

20. Below is a plot of Tolman electronic parameter and Tolman cone angle of five selected phosphines: P^tBu_3 (^tBu = *tert*-butyl), PPh_3 (Ph = phenyl), PF_3, PMe_3, and $P(C_6F_5)_3$ (C_6F_5 = pentafluorophenyl). Which of the following choices is the correct combination?

    (A) A: PF_3, B: PMe_3, C: PPh_3, D: P^tBu_3, E: $P(C_6F_5)_3$

    (B) A: PMe_3, B: PF_3, C: PPh_3, D: $P(C_6F_5)_3$, E: P^tBu_3

    (C) A: PMe_3, B: PF_3, C: PPh_3, D: P^tBu_3, E: $P(C_6F_5)_3$

    (D) A: PMe_3, B: PF_3, C: P^tBu_3, D: PPh_3, E: $P(C_6F_5)_3$

    (E) A: PF_3, B: PMe_3, C: $P(C_6F_5)_3$, D: PPh_3, E: P^tBu_3

二、問答題：（60分）

21. Consider the hypothetical linear molecule, $H_3C-Ni-CH_3$: (16%)

    (a) Draw a qualitative molecular orbital diagram for the complex $H_3C-Ni-CH_3$. Remember that the z axis should be the unique axis. Provide an appropriate label for each molecular orbital, sketch each molecular orbital, and fill in the electrons and predict the bond order for this molecule. (7%)

    (b) Draw a qualitative d-orbital splitting diagram for $H_3C-Ni-CH_3$ using a crystal field theory approach. Remember to label d-orbitals and indicate the energy barycenter. (7%)

    (c) Do your answers to parts (a) and (b) agree? Briefly explain why or why not. (2%)

22. A given transition metal complex, ML_n, forms only a dihydrogen complex $L_nM(\eta^2\text{-}H_2)$, not a true oxidative addition product $L_nM(H)_2$ with H_2. Would the true oxidative addition product be more of less likely to form as we move … (12%) Note: for (a)–(d), provide a one-sentence explanation.

    (a) To more electron donating ligands? (2%)

    (b) From a third-row to a first-row metal? (2%)

    (c) To the 1-electron oxidation product, $[L_nM(\eta^2\text{-}H_2)]^+$? (2%)

    (d) The same metal fragment, ML_n, is also used to react with ethylene, C_2H_4, to form the resulting product, $L_nM(C_2H_4)$. Would you expect a predominantly Dewar-Chatt-Duncanson structure or a complex with a metallacyclopropane fragment? (2%)

    (e) Following question (d), assuming n = 5, draw the molecular structures (with correct geometric representation) of both "Dewar-Chatt-Duncanson" and "metallacyclopropane". (4%)

23. State which complex has the larger diameter and briefly give your reasoning. (12%)

    (a) $[Co(H_2O)_6]^{3+}$ or $[Co(H_2O)_6]^{2+}$. (4%)

    (b) $[Fe(H_2O)_6]^{3+}$ or $[Cr(H_2O)_6]^{2+}$. (4%)

    (c) Low-spin $[Co(H_2O)_6]^{2+}$ or high-spin $[Co(H_2O)_6]^{2+}$. (4%)

24. What are the two lowest energy electronic absorption transitions that you expect to observe for the complex $[Ni(H_2O)_6]^{2+}$? Indicate the metal's oxidation state and d-electron count also. (10%)

25. Give two methods of measuring the magnetic properties of molecules (for example, a transition metal complex or an organic radical) and briefly explain how they work. (10%)

Character tables

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)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
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		
E_g	+2	−1	0	0	+2	+2	0	−1	+2	0		$(2z^2-x^2-y^2,\ x^2-y^2)$
T_{1g}	+3	0	−1	+1	−1	+3	+1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	+3	0	+1	−1	−1	+3	−1	0	−1	+1		(xz, yz, xy)
A_{1u}	+1	+1	+1	+1	+1	−1	−1	−1	−1	−1		
A_{2u}	+1	+1	−1	−1	+1	−1	+1	−1	−1	+1		
E_u	+2	−1	0	0	+2	−2	0	+1	−2	0		
T_{1u}	+3	0	−1	+1	−1	−3	−1	0	+1	+1	(x, y, z)	
T_{2u}	+3	0	+1	−1	−1	−3	+1	0	+1	−1		

$D_{\infty h}$	E	$2C_\infty$	…	$\infty\sigma_v$	i	$2S_\infty$	…	$\infty C''_2$		
Σ_g^+	+1	+1	…	+1	+1	+1	…	+1		$x^2+y^2,\ z^2$
Σ_g^-	+1	+1	…	−1	+1	+1	…	−1	R_z	
Π_g	+2	$+2\cos(\varphi)$	…	0	+2	$-2\cos(\varphi)$	…	0	(R_x, R_y)	(xz, yz)
Δ_g	+2	$+2\cos(2\varphi)$	…	0	+2	$2\cos(2\varphi)$	…	0		$(x^2-y^2,\ xy)$
Φ_g	+2	$+2\cos(3\varphi)$	…	0	+2	$-2\cos(3\varphi)$	…	0		
E_{ng}	+2	$+2\cos(n\varphi)$	…	0	+2	$(-1)^n 2\cos(n\varphi)$	…	0		
…	…	…	…	…	…	…	…	…		
Σ_u^+	+1	+1	…	+1	−1	−1	…	−1	z	
Σ_u^-	+1	+1	…	−1	−1	−1	…	1		
Π_u	+2	$+2\cos(\varphi)$	…	0	−2	$+2\cos(\varphi)$	…	0	(x, y)	
Δ_u	+2	$+2\cos(2\varphi)$	…	0	−2	$-2\cos(\varphi)$	…	0		
Φ_u	+2	$+2\cos(3\varphi)$	…	0	−2	$+2\cos(3\varphi)$	…	0		
E_{nu}	+2	$+2\cos(n\varphi)$	…	0	−2	$(-1)^{n+1}2\cos(n\varphi)$	…	0		
…	…	…	…	…	…	…	…	…		

Tanabe-Sugano diagram for octahedral complexes with d⁸ electron configuration