編號： 48

國立成功大學 105 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：0228，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、選擇題：(60 分，每題 3 分)

1. What is the shape of TeF_4? (a) tetrahedral　(b) pyramidal　(c) seesaw　(d) square planar

2. Decide the point group of $[Fe(py)_6]^{2+}$. The iron has the expected regular octahedral environment of six nitrogen atoms about it with the pyridine molecules lying in three mutually perpendicular planes and with each pair of trans pyridine rings coplanar. (a) O_h　(b) D_{4h}　(c) D_{2h}　(d) T_h

3. Decide the point group for (δ, δ) *trans*-$[Co(en)_2Cl_2]^+$, where both ethylenediamine are δ conformations.
(a) C_2　(b) D_2　(c) C_{2h}　(d) D_{2h}

4. For XeF_4, determine the number of bands for Xe-F stretching in IR spectrum and Raman spectrum.
(a) IR: 1, Raman: 1　(b) IR: 2, Raman: 2　(c) IR: 1, Raman: 2　(d) IR: 2, Raman: 1

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)	

5. Which one is most soluble in water? (a) $PbCl_2$　(b) PbS　(c) $PbBr_2$　(d) PbI_2

6. Arrange the value of pKa(H_2O) for $HCo(CO)_3L$: I. L = CO, II. L= PPh_3, III. L= $P(OPh)_3$
(a) I > II > III　(b) II > I > III　(c) II > III > I　(d) III > II > I

7. Which of the following lattices has two lattice points per unit cell?
(a) primitive triclinic (b) primitive tetragonal　(c) face-centered orthorhombic　(d) end-centered cubic

8. Which of the following salts has the largest lattice enthalpy? (a) LiF　(b) CsF　(c) CsI　(d) LiI

9. Predict the number of unpaired electron of $[Ir^{IV}(Mes)_4]$, Mes = 2,4,6-trimethylphenyl.
(a) 0　(b) 1　(c) 4　(d) 5

10. Arrange the LMCT band for the following compounds: I. MnO_4^{2-}; II. MnO_4^- and III. TcO_4^-
(a) I > II > III　(b) II > I > III　(c) II > III > I　(d) III > II > I

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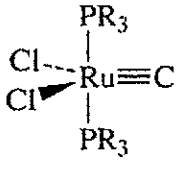
11. For the reaction, *trans*-$Pt(py)_2Cl_2 + Y \rightarrow$ *trans*-$Pt(py)_2ClY + Cl^-$, which incoming ligand, Y, leads to more rapid ligand exchange? (a) PPh_3 (b) NH_3 (c) N_3^- (d) I^-

12. The redox reaction: $[(NH_3)_5CoX]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow Co^{2+} + 5\ NH_3 + [Cr(H_2O)_5X]^{2+} + H_2O$, which ligand, X^-, leads to more rapid of redox? (a) NO_3^- (b) F^- (c) Cl^- (d) I^-

13. For the reaction, $[(NH_3)_5CoL]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow Co^{2+} + 5\ NH_3 + [Cr(H_2O)_5L]^{2+} + H_2O$, which ligand, L, leads to more rapid of redox?

(a) $CH_3C(=O)-O^-$ (b) $HOCH_2C(=O)-O^-$ (c) $O=CHC(=O)-O^-$ (d) $C_6H_5C(=O)-O^-$

14. Arrange the energy of ν_{CO} for *fac*-$Mo(CO)_3L_3$: I. L = PF_3, II. L= PCl_3, III. L= PMe_3
(a) I > II > III (b) II > I > III (c) II > III > I (d) III > II > I

15. Determine the valance electron counts for complex  (a) 15 (b) 16 (c) 17 (d) 18

16. Which L dose likely lead to more rapid ligand dissociation: *cis*-$[Mo(CO)_4L_2] + CO \rightarrow Mo(CO)_5L + L$?
(a) PMe_3 (b) PMe_2Ph (c) $PMePh_2$ (d) PPh_3

17. Which is Grubbs catalyst used in olefin metathesis?
(a) $[RuCl_2(PCy_3)_2(=CHPh)]$ (b) $[HCo(CO)_4]$ (c) $[RhCl(PPh_3)_3]$ (d) *trans*-$Ir(CO)Cl(PEt_3)_2$

18. What is the metal bond order for $[CpFe(\mu\text{-}NO)_2FeCp]$ ($Cp = C_5H_5^-$)? (a) 0 (b) 1 (c) 2 (d) 3

19. Decide the expected structure of $Fe_4C(CO)_{13}$. (a) *Nido* (b) *Arachno* (c) *Hypho* (d) *Closo*

20. Decide the isolobal fragments for I, $Ni(PPh_3)_2$ and II, $Cu(\eta^5\text{-}C_5H_5)$, respectively.
(a) C CH_2 (b) CH CH_3 (c) CH_2 CH_2 (d) CH_3, CH_3

二、簡答題：(40 分)

1. For complexes I. $[Fe(CN)_6]^{2-}$ and II. $[Mn(H_2O)_6]^{3+}$,
   a. Describe the electron configuration under octahedron coordination for both complexes. (4%)
   b. Predict whether these complexes would be labile or inert. (2%)
   c. Decide the ground term symbol under octahedron coordination for $[Mn(H_2O)_6]^{3+}$. (2%)
   d. Calculate the crystal field stabilization energy in Dq values for $[Fe(CN)_6]^{2-}$. (2%)

2. For the π-molecular orbitals of NO_3^-:

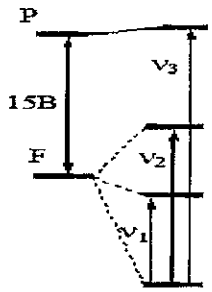
(a) Construct a representation using the pz orbital of oxygen as a basis. (2%)

(b) Reduce this to its component irreducible representations. (2%)

(c) Construct the π-molecular orbitals (NO_3^-), and the corresponding energy level diagram by using "symmetry-adapted linear combination of atomic orbitals". (6%)

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)

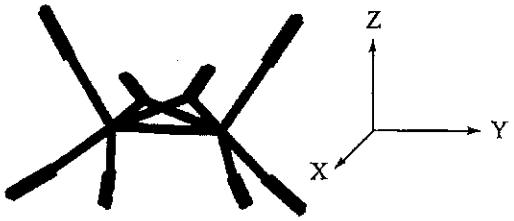
3.



For $[Ni(H_2O)_6]^{2+}$ complex displayed ν_1, ν_2, and ν_3 at 8.6 kK, 15.4 kK and 26.0 kK, respectively. (each 2%)

a. Calculate the spin-only magnetic moment (μ_B) for $[Ni(H_2O)_6]^{2+}$.
b. What is the value of wavelength in nm for 25 kK?
c. Calculate Δ_o in kK.
d. Calculate the value of 15B in kK.
e. Find the term symbols for the ground and excited state for ν_2 absorption band.

4. The solid state of $Co_2(CO)_8$ conforms to C_{2V} symmetry with two bridging CO and six terminal CO groups.



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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

(a) What are the stretching vibraion symmetries of the two bridging CO groups? (2%)

(b) What are the stretching vibration symmetries of the six termial CO gorups? (4%)

(c) When $Co_2(CO)_8$ was dissolved in solution, its structure conformed to D_{3d} symmetry. Descride the D_{3d} stucture of $Co_2(CO)_8$ and the changes of the CO stretching region in IR spectrum. (4 %)