國立成功大學 108 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：0224，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 (每題 4 分)

1. Which of the following statements is **false**?

a) superoxide has a bond order of one half (B.O.= 0.5) b) peroxide has a bond order of one (B.O.= 1) c) NO^+ has a bond order of three (B.O.= 3) d) NO^- has a bond order of two (B.O.= 2) e) dioxygenyl has a bond order of two and one half (B.O.= 2.5)

2. Predict which of the following complexes has the lower energy of CO stretching frequency.

a) $[V(CO)_6]^-$ b) $[Mn(CO)_6]^+$ c) $Cr(CO)_6$ d) $[Ti(CO)_6]^{2-}$ e) $[Fe(CO)_6]^{2+}$

3. Which of the following statements is true?

a) Arrhenius concept for acid-base definition works well for nonaqueous solution.

b) According to Bronsted-Lowry Concept for acid-base, NO_2^- is a base because it has a tendency to gain proton.

c) In solvent system concept, KF is considered as an acid in BrF_3.

d) In Lewis concept, Ag^+ can not act as an acid.

e) In Frontier orbital concept, the reaction of BF_3 and NH_3 is the interaction between HOMO of BF_3 and LUMO of NH_3.

4. Predict which way of the following reactions will go to the left, but not to the right.

a) $HI + NaF = HF + NaI$

b) $CoBr_2 + HgF_2 = CoF_2 + HgBr_2$

c) $CuI_2 + 2CuF = CuF_2 + 2CuI$

d) $ZnO + 2\ LiC_4H_9 = Zn(C_4H_9)_2 + Li_2O$

e) $TiF_4 + 2TiI_2 = TiI_4 + 2TiF_2$

5. Regarding to $[Co(ethylenediamine)_3]^{3+}$, which of the following statements is **false**?

a) the complex is optical active

b) the complex does not contain symmetry element of mirror plane

c) the point group of this complex is C3

d) the complex is a diamagnetic species if ethylenediamine is a strong-field ligand

e) ethylenediamine is a bidentate ligand and forms a five-member chelate ring when it binds to a cobalt ion.

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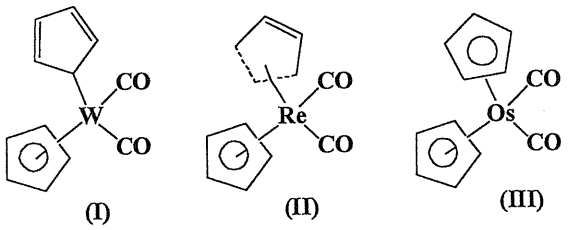
二、簡答題 (每題 3 分)

Please answer questions 1-3 related to the following three compounds.



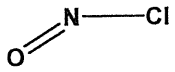
(I)　(II)　(III)

1. Determine the valence electrons for compound III.

2.How many sets of peaks (do not consider hyperfine interaction) might appear in ^{1}H NMR at low temperature in compound II

3. ^{1}H NMR at low temperature in compound I shows four sets of peaks. Please write down the ratio of intensity for these four peaks.

4. Please indicate the point group of the molecule on the right.



5. Please indicate the point group of $Fe(C_5H_5)_2$ with the staggered form

6. Determine the ground term for a high-spin d^7 configuration in O_h symmetry.

7.Use the following information to find the potential for the NO → N_2O reaction.
NO → N_2 ε^o (potential) = 1.68 V　N_2O → N_2　ε^o (potential) = 1.77 V

8. Using the Born-Harbor cycle to calculate the enthalpy of formation of LiF(s).
Use these data in the calculation: F_2 bond energy (dissociation energy) is 158 kJ/mol. The sublimation energy of Li(s) to Li(g) is 161 kJ/mol. The ionization energy of $Li_{(g)}$ to $Li^+_{(g)}$ is 520 kJ/mol. The electron affinity of $F_{(g)}$ to $F^-_{(g)}$ is 328 kJ/mol. The lattice enthalpy of $LiF_{(s)}$ is -950 kJ/mol

9. What is the number of atoms in each unit cell of the body-centered cubic structure?

10.What are Lattice points of the body-centered cubic structure?

11. Please predict the base strength in the gas phase of a) $NHMe_2$, b) NH_2Me, c) NMe_3 and d) NH_3 in an increasing order.

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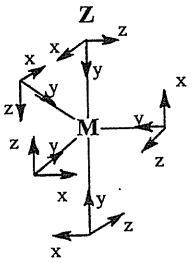
Questions 12-14 are related to constructing molecular orbitals of $[Co(Cl)_5]^{2-}$ with a trigonal bipyramidal geometry.

D3h	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A1'	1	1	1	1	1	1		x^2+y^2, z^2
A2'	1	1	-1	1	1	-1	Rz	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2,xy)
A1"	1	1	1	-1	-1	-1		
A2"	1	1	-1	-1	-1	1	z	
E"	2	-1	0	-2	1	0	(Rx,Ry)	(xz,yz)



12. The p_x and p_z sets of ligand orbitals are used in π bonding with metal ion. The derived characters of the reducible representations of p_x and p_z sets of ligand orbitals for π bonding are in the table. Please write down the value (a, b, c, d, e, f)

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{x,z}$	a	b	c	d	e	f

13. What are component irreducible representations for the reducible representations above?

14. What are the d orbitals which might have π interactions with ligands?

15 The $4f_{z(x2-y2)}$ orbital has the angular function $y = (constant)z(x^2-y^2)/r^3$. Please write down the three equations to define the angular nodal surfaces.

16. Please write down the equation for producing hydrogen gas in industry

17. Please use Lewis electron-dot methods to draw three resonance structures for thiocyanate, SCN^-.

18. What is the energy level diagrams of d-orbitals for transitional metal complexes with trigonal bipyramidal geometry? Please also label orbitals.

19. If a transition metal complex has a d^6 electrons with a trigonal bipyramidal geometry, please predict the electronic spin-state of this complex.

20. Continuing the question above, what is the calculated spin-only magnetic moment for this complex? $\mu_s = g[S(S+1)]^{1/2}$, g is the gyromagnetic ratio 2.00023

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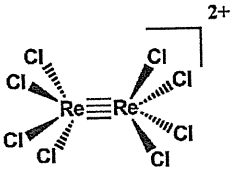
三. 詳答題

1. The isoelectronic ions VO_4^{3-} , CrO_4^{2-} , MnO_4^- all have intense charge-transfer transition bands. The wavelengths of these transitions increase in this series, with MnO_4^- having its charge-transfer absorption at the longest wavelength. Please explain this trend. (5%)

2.Please **sketch** the σ, π, and δ bonding interactions between two metal d orbitals in $[Re_2Cl_8]^{2-}$ on the right figure.(5%)



3.Please predict IR bands for CO stretching modes in cis-$ML_2(CO)_2$ and trans-$ML_2(CO)_2$. L is a monodentate ligand. Please show the process of your answer including the following three points.

a) the point groups of cis-$ML_2(CO)_2$ and trans-$ML_2(CO)_2$ (2%)

b) the symmetry irreducible representations for CO stretching modes in these two complexes. (4%)

c) the number of IR bands for CO stretching modes in these two complexes. (4%)

C_{2v}	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
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	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratic
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	