國立成功大學 82 學年度化學研究修試(無稱 化學試題)共 2月

- 1. Give the chemical formula for the names of ligands, commonly used in transition-metal complexes: (a) azide (b) aquo (c) carbonyl (d) nitrosyl (e) en; and then draw simple plausible structures for complexes with the following empirical formula: (f) $(OC)_3Re(PMe_3)$, (g) $(OC)_3Cr(C_6H_5)_2$, (h) $(OC)_2RhCl$, (i) $Mo(CO)_3(NO)_3$ (a-e; 1% each and f-i, 2% each) 13%
- 2. Choose and explain: 12%
- (a) Smaller v(CO) band in the IR spectrum of $[Fe(CO)_4]^{2-}$ or $[Ni(CO)_4]$.
- (b) Longer C-C bond distance for the uncoordinated C_2H_4 molecule or that in $[\eta^2-(C_2H_4)PtCI_3]^-$.
- (c) One or two singlets can be observed in the $^{13}\mathrm{C}$ NMR spectrum of the trigonal bipyramidal complex, Fe(CO)₅ at room temperature.
- 3. 連達看Which structural information fits which molecule or ions? (10%)
- (a) O_2 (b) NO (c) HCN (d) N_3^- (e) $[PCI_4]^-$ (f) $XeOF_4$
- (i) It is paramagnetic with one unpaired electron.
- (ii) It is isoelectronic and isostructural with ${\rm CO_2}$, although it is an ion.
- (iii) It has only a double bond.
- (iv) It has four C₃ symmetrical axes.
- (v) It is very toxic and linear.
- (vi) It increases more weight than any other species when an external magnetic field is present.

Please use the following format:

Answer	: (a)	(b)	(c)	(d)	(e)-	(f)
in your	answer sheet.				•	,

- 4. Give "yes" or "no" for each of the following complexes to show that it has probably the Jahn-Teller distortion: (a) $Cu(OH_2)_6^{2+}$ (b) $Fe(NH_3)_6^{3+}$ (c) $Cr(CN)_6^{4-}$ (d) $Mn(OH_2)_6^{2+}$ (e) $CoCl_4^{2-}$ (答錯倒扣) (5%)
- 5. Assume that, in another universe, the values of the quantum number, m_I , are limited to zero or positive integers up to the value of I for a particular subshell; thus for I=2, m_I could be 0, 1, or 2. Describe the electron configuration of nitrogen and that of Ni $^{2+}$. How many unpaired electrons would be contained in N and Ni $^{2+}$? What are the ground-state terms for N and Ni $^{2+}$ (10%)

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- 6. Draw the structures of the following: (6%) (a) BeCl $_2$ (crystal) (b) B $_4$ H $_{10}$ (c) P $_3$ O $_{10}$ 5 -
- 7. Choose and explain: (12%)
- (a) Larger bond angle: NO₂ or NO₂.
- (b) Stronger Lewis base: $(CH_3)_2O$ or $(SiH_3)_2O$.
- (c) More soluble in water: LiF or Lil.
- 8. Explain each of the following: (20%)
- (a) $Mn(OH_2)_6^{2+}$ is much less intensely colored than $Cr(OH_2)_6^{2+}$ or $Fe(OH_2)_6^{2+}$.
- (b) In aqueous solution, the order of base strength is Me $_2$ NH>MeNH $_2$ > Me $_3$ N > NH $_3$.
- (c) Pure iodine is purple in color as is its solution in CCI₄. Solutions of iodine in acetone and diethyl ether are brown.
- (d) Two separate water exchange rates are found for $Cu(OH_2)_6^{2+}$ in queous solution.
- 9. Find the number, and symmetry species, of the infrared and Raman active vibrations of trans-N₂F₂ (C_{2h}). (6%)

C _{2h}	Ε	c ₂	i	σ_{h}		
Ag	1	1	1	1	R _z	x^2 , y^2 , z^2 , xy
Bg	1	- 1	1	- 1	R _x , R _y	xz, yz
A _u	1	1	- 1	- 1	z	
B _u	1	- 1	- 1	1	x, y	

10. The reaction of $V(CO)_5(NO)$ with $P(OMe)_3$ to give $V(CO)_4\{P(OMe)_3\}(NO)$ has the rate law $-d[V(CO)_5(NO)]/dt = k_1 [V(CO)_5(NO)] + K_2 [V(CO)_5(NO)][P(OMe)_3]$ Suggest mechanisms for this reaction consistent with the rate law. (6%)