89 學年度 國立成功大學 化學研究 系 無機化學 試題 第 1 頁

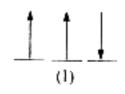
- Draw the molecular structure and determine the point group for each of the following species

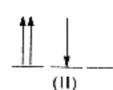
 (a) PF₃Cl₂ (b) POF₃ (c) Al₂Br₆ (gas phase) (d) Fe(C₃H₅)₂(staggered) (e) [ReH₉]²:
- The point group of trigonal bipyramid Fe(CO)₅ is D₃₆. The character table of D₃₆ is shown below. 10%

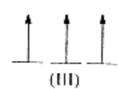
| D_{3h} | E | 2C3 | 3C ₂ | σ_h | 28, | $3\sigma_{\rm v}$ | 1 |
|-------------|---|-----|-----------------|------------|-----|-------------------|-------------------------------|
| A_i | 1 | 1 | 1 | 1 | ı | | $x^2 + v^2$, z^2 |
| A_{j} | 1 | ı | -1 | 1 | 1 | -1 | / |
| $E^{'}$ | 2 | -1 | 0 | 2 | -1 | 0 | $(x,y) = (x^2 \cdot y^2, xy)$ |
| A_{I}^{-} | 1 | 1 | ı | -1 | -1 | -1 | |
| A_2 | ı | 1 | - ì | -1 | -1 | ı | 2 |
| $E^{"}$ | 2 | -1 | 0 | -2 | 1 | 0 | (xz,yz) |

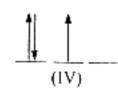
- (a) What are the traces of the reducible representation for the five Fe-C σ orbitals?
- (b) What are the irreducible representations for the five Fe-C σ orbitals?
- (c) Determine what atomic orbitals of Fe are allowed by symmetry to be used in the construction of σ hybrid orbitals.
- 3 Consider the following possible electron arrangements for a p^3 configuration.

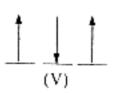
10%











- (a) Which of these represents the ground state? Determine the term symbol for the ground state
- (b) Which is impossible state?
- (c) In which configuration would exchange energy be maximized?
- (d) In which configuration would columbic repulsion be maximized?
- (e) Determine the number of microstates for a p^{j} configuration.
- 4 Choose and explain

24%

- (a) Which has no mismatch of the sign of the wave function in the π system?
- (PNCl₂)₄ or (PNCl₂)₃ (b) Which is the more stable complex?

 $[O_2][PtF_6]$ or $[N_2][PtF_6]$

(c). Which has less intensity of d-d transition in visible range?

 $[Fe(H_2O)_6]^{2+}$ or $[Mn(H_2O)_6]^{2+}$

(d). Which will exhibit the greater polarizing power?

Ti²' or Ti⁴

(e) Which has the higher boiling point?

Ni(CO)₄ or CCl₄

(f) Which has the higher energy Cr-C stretching bands in the infrared spectrum?

 $[Cr(CO)_5(PF_3)]$ or $[Cr(CO)_5(PCI_1)]$

- [Fe(phen)₂(SCN)₂] behaves as a spin-crossover complex, below Tc (critical temperature) only the 16% low spin phase is present and above Tc only the high spin phase is present.
 - (a) What is the main driving force in spin crossover transformation?
 - (b) What is relationship between the crystal field splitting energy (Δ_o) and the main spin pairing energy (Π)?
 - (c) What is the electron configuration for the high spin phase? What is the spin-only effective magnetic moment (μ_{eff}) for the high spin phase? Calculate the LFSE for the high spin phase.
 - (d) What is the electron configuration for the low spin phase? What is the spin-only effective magnetic moment (μ_{eff}) for the low spin phase? Calculate the LFSE for the low spin phase.
- 6 Draw out all the isomers (geometric isomers, and enantiomers) for [Co(bipy)(NH₁)₂Cl₂]*.
 Assign the absolute configuration (Δ and Λ) of the enantiomers

- Predict the geometries of the complexes which result from the following reactions
 (a) [Pt(NO₂)Cl₃]² + NH₃ → [Pt(NO₂)(NH₃)Cl₂] + Cl²
 - (b) cis-[Pt(RNH₂)₂(NH₃)(NO₂)]' + CT \rightarrow [Pt(RNH₂)(NH₃)(NO₂)Cl] + RNH₂
- Predict whether these complexes would be labile or inert and explain your choices
 (a) Potassium hexaiodomanganate(IV)
 - (b) Potassium hexacyanoferrate(III)
- 10 Which of the following obey the 18-electron rule?
 - (a). Fe(CO)₅
 - (b). $[Rh(bipy)_2CI]'$
 - (c) (Cp*)ReO₃
 - (d). $Os(CO)(\equiv CPh)(PPh_3)_2CI$