國立成功大學
115學年度碩士班招生考試試題

編　號：37

系　所：化學系

科　目：無機化學

日　期：0203

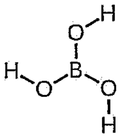
節　次：第 3 節

注　意：1.不可使用計算機
　　　　2.請於答案卷(卡)作答，於試題上作答，不予計分。

一、單選題：（50 分，每題 2 分）

1. Metal-Organic Frameworks, the subject of the 2025 Nobel Prize in Chemistry, are best described by which structural characteristic?
   (A) Long protein chains folded into enzymatic shapes.
   (B) Two-dimensional sheets of carbon atoms arranged in a honeycomb lattice.
   (C) Porous crystalline materials composed of metal nodes linked by organic ligands.
   (D) Dense metallic alloys with high conductivity.
   (E) Amorphous solids with random atomic arrangements.

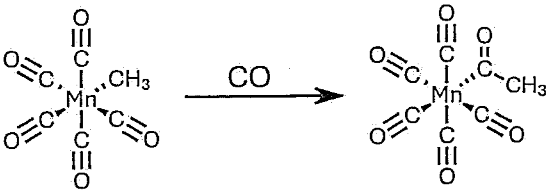
2. Determine the point group of boric acid, H_3BO_3.
   (A) C_{3v} (B) D_{3h} (C) D_{3d} (D) C_{3h} (E) C_3



3. Why is boric acid classified as an acid in aqueous solution?
   (A) It dissociates to release one of its own H^+ ions from a hydroxyl group.
   (B) It acts as a Lewis acid by accepting an OH^- ion from water, effectively releasing a proton.
   (C) It contains three replaceable hydrogen atoms that all dissociate simultaneously.
   (D) It is not acid.
   (E) It reacts with bases to form salt and water through a simple neutralization of its H atoms.

4. Using the flowchart for determining the point group. What is the next step if the molecule does not contain n perpendicular C_2 axes?
   (A) Does the molecule contain a horizontal reflection plane (σ_h)?
   (B) Does the molecule contain n dihedral reflection planes (σ_d)?
   (C) Does the molecule contain a reflection plane?
   (D) Does the molecule contain a proper rotation axis (C_n)?
   (E) Does the molecule contain n vertical reflection planes (σ_v)?

5. What is the following reaction mechanism?



   (A) Oxidative insertion (B) Reductive elimination (C) Migratory insertion
   (D) Transmetallation (E) Substitution

6. The atomic radius of aluminum (Al) is 143 pm, while that of gallium (Ga) is 122 pm. Why is Al larger than Ga, despite Ga being below Al in Group 13?
   (A) Ga is a transition metal, which inherently has a smaller radius than p-block elements like Al.
   (B) The addition of the 3d subshell in Ga provides poor shielding, leading to a higher effective nuclear charge that pulls valence electrons closer.
   (C) Al has more electron shells occupied than Ga, causing its atomic radius to be larger.
   (D) Ga has a more stable electron configuration that allows its valence shell to contract more easily than Al's.
   (E) Ga is larger than Al.

7. What is the total number of electrons that can be in level $n = 5$?
   (A) 32 (B) 2 (C) 50 (D) 8 (E) 18

8. The valence electron configuration of an element is $ns^2(n-1)d^{10}np^2$. Which group does this element belong to?
   (A) 13 (B) 14 (C) 15 (D) 16 (E) 17

9. Order the following diatomic molecules from the shortest to longest bond: C_2, B_2, H_2, N_2.
   (A) N_2, C_2, B_2, H_2 (B) C_2, N_2, H_2, B_2 (C) H_2, N_2, C_2, B_2 (D) C_2, B_2, H_2, N_2 (E) H_2, N_2, B_2, C_2

10. Vibrational transitions in a given molecule typically require energies that correspond to which region of the electromagnetic spectrum?
    (A) Visible (B) UV (C) IR (D) X-ray (E) microwave

11. In palladium-catalyzed cross-coupling reactions, such as the Suzuki-Miyaura coupling or Heck reaction, why is the addition of a base typically essential?
    (A) To increase the oxidation state of the palladium catalyst from Pd(0) to Pd(II) to initiate oxidative addition.
    (B) To activate the organometallic nucleophile or to neutralize the hydrogen halide (HX) generated during the catalytic cycle.
    (C) To serve as a sacrificial oxidant that prevents the palladium from precipitating as palladium black.
    (D) To act as a bulky ligand that occupies coordination sites on the palladium to prevent over-reaction.

12. Which of the following energy terms in the Born-Haber cycle for the formation of $NaCl_{(s)}$ is typically an exothermic process?
    (A) Enthalpy of sublimation of $Na_{(s)}$ (B) Second ionization energy of $Na_{(g)}$
    (C) First ionization energy of $Na_{(g)}$ (D) First electron affinity of $Cl_{(g)}$
    (E) Bond dissociation enthalpy of $Cl_{2(g)}$

13. In the solid state, why does cesium chloride (CsCl) adopt a coordination number of 8 while sodium chloride (NaCl) adopts a coordination number of 6?
    (A) The lattice energy of NaCl is higher than that of CsCl.
    (B) Cesium is more electronegative than sodium.
    (C) NaCl forms a body-centered lattice while CsCl forms a face-centered lattice.
    (D) The larger size of the Cs^+ cation allows more Cl^- ions to surround it without anion-anion repulsion.
    (E) NaCl is more covalent in nature than CsCl.

14. What is the shape of SF_4?
    (A) Tetrahedral (B) Square planar (C) Seesaw (D) Trigonal pyramidal (E) Square pyramidal

15. According to the Hard-Soft Acid-Base (HSAB) theory, which of the following reactions is most likely to have an equilibrium constant (K) much greater than 1?
    (A) $AlF_3 + 3\,AgI \rightleftharpoons AlI_3 + 3\,AgF$
    (B) $TiCl_4 + 4\,LiI \rightleftharpoons TiI_4 + 4\,LiCl$
    (C) $HgI_2 + CaF_2 \rightleftharpoons HgF_2 + CaI_2$
    (D) $CuI + NaCl \rightleftharpoons CuCl + NaI$
    (E) $AgF + LiI \rightleftharpoons AgI + LiF$

16. The Lewis acidity of boron trihalides follows the trend: $BF_3 < BCl_3 < BBr_3$. What is the primary reason for this unexpected order?
(A) The 3p and 4p orbitals of Cl and Br are too small to overlap with B.
(B) Electronegativity decreases from F to Br, making B more positive in BBr_3.
(C) BBr_3 has a higher bond dissociation energy than BF_3.
(D) The π-bonding between the halogen and B is most effective in BF_3.
(E) Steric effect in BBr_3 is lower than that in BF_3.

17. Which of the following complexes can exist as a pair of *fac* and *mer* isomers? (en = ethylenediamine)
(A) $[Co(NH_3)_4Cl_2]^+$ (B) $[Fe(CN)_5(NO)]^{2-}$ (C) $[Cr(en)_3]^{3+}$ (D) $[Co(NH_3)_3(NO_2)_3]$ (E) $[Pt(NH_3)_2Cl_2]$

18. The complex $[Co(en)_2Cl_2]^+$ exists as several isomers. Which of the following statements is correct regarding its stereochemistry?
(A) The *cis* isomer is a *meso* compound and is optically inactive.
(B) The *cis* isomer is chiral and exists as a pair of enantiomers (Δ and Λ).
(C) The *trans* isomer is chiral and has a non-superimposable mirror image.
(D) The complex can only exist as structural isomers, not stereoisomers.
(E) Both the *cis* and *trans* isomers are optically active.

19. Which of the following describes the correct d-orbital splitting pattern in a square planar crystal field, from lowest energy to highest?
(A) $d_{x^2-y^2} < d_{xy} < d_{z^2} < d_{xz}, d_{yz}$
(B) $d_{z^2} < d_{xz}, d_{yz} < d_{xy} < d_{x^2-y^2}$
(C) $d_{xy} < d_{z^2} < d_{xz}, d_{yz} < d_{x^2-y^2}$
(D) $d_{xz}, d_{yz} < d_{z^2} < d_{x^2-y^2} < d_{xy}$
(E) $d_{xz}, d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$

20. In the molecular orbital diagram of an octahedral complex, how does π-backbonding from the metal to a ligand like CO affect the value of Δ_{oct}?
(A) It increases Δ_{oct} by increasing the repulsion between ligands.
(B) It increases Δ_{oct} by lowering the energy of the t_{2g} orbitals.
(C) It has no effect on Δ_{oct} as π-bonding only involves $e_g{}^*$ orbitals.
(D) It decreases Δ_{oct} by lowering the energy of the $e_g{}^*$ orbitals.
(E) It decreases Δ_{oct} by raising the energy of the t_{2g} orbitals.

21. Why are Tanabe-Sugano diagrams often preferred over Orgel diagrams for interpreting the spectra of d^2 to d^8 complexes?
(A) Orgel diagrams are only used for d^0 and d^{10} systems.
(B) Orgel diagrams do not include spin-allowed transitions.
(C) Tanabe-Sugano diagrams are simpler because they ignore electron-electron repulsions.
(D) Tanabe-Sugano diagrams treat the Racah parameter B as a variable, allowing for the inclusion of both high-spin and low-spin states.
(E) Orgel diagrams are only valid for tetrahedral complexes.

22. What is the major product formed when $[PtCl_4]^{2-}$ reacts with one equivalent of NH_3, followed by one equivalent of NO_2^-?
(A) *fac*-$[PtCl_3(NH_3)(NO_2)]^-$ (B) *cis*-$[PtCl_2(NO_2)_2]^{2-}$ (C) *cis*-$[PtCl_2(NH_3)(NO_2)]^-$
(D) $[Pt(NH_3)_2(NO_2)_2]$ (E) *trans*-$[PtCl_2(NH_3)(NO_2)]^-$

23. In the reaction $[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{2+} + [Cr(H_2O)_5Cl]^{2+}$, the chloride ion ends up attached to Cr. This is classic evidence for which mechanism?
(A) Inner-sphere electron transfer (B) Outer-sphere electron transfer
(C) Berry pseudorotation (D) Associative ligand substitution
(E) Reductive elimination

24. The complex $Co_2(CO)_8$ exists in different isomeric forms. In the solid state, it contains two bridging CO ligands. How many Co–Co bonds are required to satisfy the 18-electron rule for each Co atom?
(A) 4 (B) 1 (C) 3 (D) 2 (E) 0

25. Wilkinson's catalyst, $RhCl(PPh_3)_3$, can be used for the selective hydrogenation of alkenes. Which statement regarding its mechanism is true?
(A) It is an example of a heterogeneous catalyst.
(B) The first step in the cycle is the coordination of the alkene to the 16-electron complex.
(C) The metal center is oxidized to Rh(II) during the oxidative addition step.
(D) The catalyst obeys the 18-electron rule in its resting state.
(E) The active species formed in solution is a 14-electron complex $RhCl(PPh_3)_2$.

二、問答題：(50 分)

26. (14 points) Consider the CO molecule:
(A) (4 points) Draw the most stable Lewis structure for this molecule. What are the oxidation states and formal charges of each element?
(B) (6 points) Construct the molecular orbital diagram of CO. Fill in the electrons and calculate the bond order. Please draw clearly to receive full credit. Use the following orbital potential energies to construct the MO diagram:

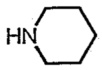
	2s	2p
C	−19.4 eV	−10.7 eV
O	−32.4 eV	−15.8 eV

(C) (4 points) Why does CO usually coordinate to the transition metal through C but not O?

27. (14 points) The complex *trans*-$PtCl_2(pip)_2$ (pip = piperidine) reacts with $NaNO_2$ in methanol to form *trans*-$PtCl(NO_2)(pip)_2$. The kinetic data for a reaction between a 0.0007 M solution of *trans*-$PtCl_2(pip)_2$ and different concentrations of $NaNO_2$ are given below. The reaction follows the rate law:

$$\text{Rate} = k_1[\textit{trans}\text{-}PtCl_2(pip)_2] + k_2[\textit{trans}\text{-}PtCl_2(pip)_2][NaNO_2]$$

$[NaNO_2]$ (M)	k_{obs} (s^{-1})
0.010	3000
0.020	5200
0.030	7400
0.040	9600



Piperidine

(A) (6 points) Write the mechanism for the substitution reaction between *trans*-$PtCl_2(pip)_2$ and $NaNO_2$.
(B) (4 points) Explain why there are two rate constants, k_1 and k_2.
(C) (4 points) Plot a graph of $[NaNO_2]$ (x-axis) against k_{obs} (y-axis) and use this to calculate k_1 and k_2.

28. (12 points) Using the 18-electron rule as a guide, indicate the probable number of carbonyl ligands in the following complexes and draw the structure as accurately as possible.
    (A) (4 points) $W(\eta^6\text{-}C_6H_6)(CO)_n$ (C_6H_6 = benzene)
    (B) (4 points) $Rh(\eta^5\text{-}C_5H_5)(CO)_n$ ($C_5H_5^-$ = cyclopentadienide)
    (C) (4 points) $Ru_3(CO)_n$ (Hint: the three Ru centers form a triangle with three Ru–Ru bonds)

29. (10 points) The chromium centers in the crystal structure of $KCrF_3$ are in an octahedral environment of fluorine atoms. Four of the Cr–F bond distances are 214 pm, and the remaining two *trans* Cr–F bond distances are 201 pm. Explain these observations and include a crystal field splitting diagram.

Trans Effect: $CN^- \sim CO \sim C_2H_4 > PH_3 \sim SH_2 > NO_2^- > I^- > Br^- > Cl^- > NH_3 \sim py > OH^- > H_2O$

Spectrochemical series: $CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$

$\mu_{\text{spin-only}} = \sqrt{4S(S+1)} = \sqrt{n(n+2)}$

1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.94	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.63	33 **As** 74.92	34 **Se** 78.97	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.95	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57/71	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89/103	104 **Rf** (267)	105 **Db** (268)	106 **Sg** (271)	107 **Bh** (272)	108 **Hs** (270)	109 **Mt** (276)	110 **Ds** (281)	111 **Rg** (280)	112 **Cn** (285)	113 **Nh** (284)	114 **Fl** (289)	115 **Mc** (288)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

57 **La** 138.9	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.2	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.2	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
89 **Ac** (227)	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)