

一、單選題 (答案請填於答案卡，答錯不倒扣，每題 2 分，共 50 分)

1. Which metal is naturally found in its elemental state?
(A) gold (B) titanium (C) chromium (D) iron (E) zinc
2. Which complex ion is diamagnetic?
(A) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (C) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (D) $[\text{CoCl}_6]^{3-}$ (E) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
3. Which orbital gives an electron a greater probability of being found closer to the nucleus?
(A) 3s (B) 2s (C) 3f (D) 3p (E) 3d
4. The metallic radii in the third row of the d block are very similar to those in the second row, and not significantly larger as might be expected given their considerably larger numbers of electrons. We name this as
(A) shielding effect (B) inert-pair effect (C) penetration (D) lanthanide contraction (E) catenation
5. The metal coordinated by porphyrin ligand called a heme is connected to a protein. Which of the following proteins is not a O_2 /[O] transport and storage proteins?
(A) myoglobin (B) hemoglobin (C) hemocyanin (D) ferritin (E) cytochrome P-450
6. The $\text{Fe}=\text{O}$ oxidizing center in cytochrome P-450 is characterized as an Fe(IV) complex with the porphyrin also oxidized by one electron. Which of the following statement is **incorrect**?
(A) The complex has a magnetic susceptibility that indicates the presence of two unpaired electrons
(B) The iron ion is in a triplet state ($S = 1$)
(C) The Fe(IV) oxidation state corresponds to t_{2g}^4 with two unpaired electrons
(D) The oxidation of the porphyrin ring removes one electron from the π HOMO
(E) Cytochrome P-450 is the enzyme with iron porphyrin active site that catalyzes the addition of oxygen to a substrate
7. The Monsanto process, a highly successful commercial process, is based on the metal-catalyzed carbonylation of methanol. This metal-containing catalyst is:
(A) $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]$ (B) $[\text{RhI}_2(\text{CO})_2]^-$ (C) $[\text{RhCl}(\text{PPh}_3)_3]$ (D) $[\text{CoH}(\text{CO})_4]$ (E) $[\text{CoH}(\text{CO})_3]$
8. A good way to picture the incorporation of hetero atoms into a metal cluster is to use isolobal analogies. Which of the following fragments is the isolobal analogy of $[\text{Mn}(\text{CO})_5]^+$?
(A) $[\text{Co}(\text{CO})_3]$ (B) $[\text{Fe}(\text{CO})_4]$ (C) $[\text{Co}(\text{CO})_4]$ (D) $[\text{HFe}(\text{CO})_3]$ (E) $[\text{NH}_2]$

9. Which of the following statement is **incorrect**?
- (A) For the Schrock carbene, the p_z orbital of CR_2 is higher in energy than the d_p orbitals of metal
(B) For the Schrock carbene, the carbene C is nucleophilic
(C) For the Schrock carbene, the $M=C$ bond is polarized so as to put negative charge on the metal-bound C atom
(D) In the Fischer carbene, the π -electron density is largely concentrated on the metal atom
(E) Fischer carbenes are attacked at the C atom by nucleophiles
10. Which of the following complexes displays one very strong IR absorption band at 1889 cm^{-1} and two other very weak bands in the CO stretching region?
- (A) $Co(CO)_4$ (B) *cis*- $[Cr(CO)_4(PPh_3)_2]$ (C) *trans*- $[Cr(CO)_4(PPh_3)_2]$ (D) $Fe(CO)_5$ (E) $Ni(CO)_4$
11. The highest occupied molecular orbital for O_2 molecule is
- (A) $\pi_g^*(2p)$ (B) $\pi_u(2p)$ (C) $\sigma_g(2p)$ (D) $\sigma_u^*(2p)$ (E) $\sigma_g(2s)$
12. Which of the following dinuclear complexes is regarded as having a quadruple bond?
- (A) $Re_2(CO)_{10}$ (B) $Fe_2(CO)_9$ (C) $Mn_2(CO)_{10}$ (D) $[Re_2Cl_{10}]^{2-}$ (E) $Co_2(CO)_8$
13. The octahedral d^3 complex $[Cr(NH_3)_6]^{3+}$ showing the absorption spectrum in the region near 25000 cm^{-1} can be identified as arising from
- (A) $d-d$ transition
(B) ligand-to-metal charge transfer
(C) metal-to-ligand charge transfer
(D) intervalence transitions
(E) intersystem crossing
14. Which of the following statement is **incorrect**?
- (A) Hyponitrite usually acts as a reducing agent
(B) Nitrite acts as an oxidizing and a reducing agent
(C) The symmetry of dinitrogen tetroxide is C_{2v}
(D) Nitrogen dioxide is a reactive and paramagnetic gas at room temperature
(E) Nitrous oxide is not very reactive gas
15. Which of the following molecules is infrared (IR) inactive in the gas phase?
- (A) N_2 (B) NO (C) NO_2 (D) CO (E) N_2O
16. The radical anion of the following conjugated hydrocarbons (from (A) to (E)) **cannot be formed** when such compounds are reacted with an alkali metal in a polar aprotic solvent
- (A) biphenyl (B) benzene (C) naphthalene (D) phenanthrene (E) anthracene

17. The most economical sources of hydrogen are the reactions of carbon, methane or carbon monoxide with water at high temperature. Which of the following reactions is called shift reaction?
- (A) $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
 (B) $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$
 (C) $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$
 (D) $\text{CH}_3\text{CH}_3(\text{g}) \rightarrow \text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2(\text{g})$
 (E) $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g})$
18. Which of the following groups of ions is classified as hard acid?
- (A) F^- , Cu^+ (B) Br^- , H^- (C) H^+ , Na^+ (D) SCN^- , H_2O (E) I^- , S^{2-}
19. On the basis of Hund's rule, which term is regarded as the ground state for a d^2 ion?
- (A) ^1G (B) ^3F (C) ^3P (D) ^1D (E) ^1S .
20. The notation for complex $[\text{Co}(\text{EDTA})]^-$ (EDTA = ethylenediaminetetracetato) is:
- (A) $\Lambda\Delta\Delta$ -(ethylenediaminetetracetato)cobaltate(III)
 (B) $\Delta\Delta\Delta$ -(ethylenediaminetetracetato)cobaltate(III)
 (C) $\Lambda\Delta\Delta$ -(ethylenediaminetetracetato)cobaltate(II)
 (D) $\Lambda\Delta\Delta$ -(ethylenediaminetetracetato)cobaltate(III)
 (E) $\Lambda\Delta\Delta$ -(ethylenediaminetetracetato)cobaltate(III)
21. The sizes of coupling constants are often related to the geometry of a molecule. In square planar Pt(II) complexes, $J(\text{Pt-P})$ is sensitive to the group *trans* to a phosphane ligand. Which of the following order is correct in terms of $J(\text{Pt-P})$?
- (A) $\text{cis-}[\text{PtCl}_2(\text{PEt}_3)_2] > \text{trans-}[\text{PtCl}_2(\text{PEt}_3)_2]$
 (B) $[\text{PtCl}_2(\text{PEt}_3)_2] < [\text{PtBr}_2(\text{PEt}_3)_2]$
 (C) $[\text{PtCl}_2(\text{PEt}_3)_2] < [\text{Pt}(\text{NH}_3)_2(\text{PEt}_3)_2]$
 (D) $[\text{Pt}(\text{NH}_3)_2(\text{PEt}_3)_2] < [\text{Pt}(\text{CH}_3)_2(\text{PEt}_3)_2]$
 (E) $[\text{PtBr}_2(\text{PEt}_3)_2] < [\text{PtH}_2(\text{PEt}_3)_2]$
22. Photochemical or thermal activation of metal carbonyls is often an effective route to introduce neutral cyclic polyene ligands into the metal coordination sphere. Predict the reaction product when hexacarbonylchromium(0) is refluxed with an arene.
- (A) $[\text{Cr}(\text{CO})_5(\text{C}_6\text{H}_4)] + \text{CO} + \text{H}_2$
 (B) $[\text{Cr}(\text{CO})_4(\text{C}_6\text{H}_2)] + 2\text{H}_2 + 2\text{CO}$
 (C) $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)] + 3\text{CO}$
 (D) $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2] + 6\text{CO}$
 (E) $[\text{Cr}(\text{CO})_4(\text{H})(\text{C}_6\text{H}_5)] + 2\text{CO}$

23. More and more people in our society seem to be suffering from the debilitating effects of mania and depression. Which of the following compounds can help to alleviate mood disorders?
 (A) Na_2CO_3 (B) K_2CO_3 (C) Li_2CO_3 (D) Rb_2CO_3 (E) FeSO_4
24. Predict the probable products of the reaction, BBr_3 and excess $\text{NH}(\text{CH}_3)_2$ in a hydrocarbon solvent.
 (A) $3\text{HBr}_{(g)} + \text{B}(\text{N}(\text{CH}_3)_2)_3$
 (B) $\text{HBr}_{(g)} + \text{B}(\text{N}(\text{CH}_3)_2)_2\text{Br}_2$
 (C) $2\text{HBr}_{(g)} + \text{B}(\text{N}(\text{CH}_3)_2)_2\text{Br}$
 (D) $[(\text{CH}_3)_2(\text{H})\text{N}-\text{BBr}_3]$
 (E) $[\text{BBr}_2][\text{BrNH}(\text{CH}_3)_2]$
25. Which of the following ligands shows the ambidentate character?
 (A) ethylenediamine (B) 2,2'-bipyridine (C) $\text{C}_2\text{O}_4^{2-}$ (D) NO_2^- (E) NH_3

二、問答題 (共 50 分)

1. On atomic structure: The least amount of energy that can be emitted by an excited electron in a hydrogen atom falling from $n = 4$ state directly to the $n = 3$ state is about $1.06 \times 10^{-19} \text{ J}$. Can this electromagnetic radiation be seen by humans? Why? (4%)
2. For the ion of dithiocarbonate, $[\text{S}_2\text{CO}]^{2-}$ (C is central), draw its resonance structures, assign formal charges, and select the resonance structure likely to provide the best description. (6%)
3. About molecular symmetry: (8%)
 (a) Determine the point group for the most likely isomer of PCl_2F_3 (3%)
 (b) What are point groups for the *cis* and *trans* isomers of IO_2F_4 ? Are infrared spectra be able to distinguish the two isomers? How? (5%)
4. About the two anionic species SCN^- and CN^- : (7%)
 (a) Give the chemical name (in English) for each of them. (2%)
 (b) SCN^- ion can form bonds with metal ions through either N or S, depending on the rest of the molecule. What is the likelihood that CN^- form bonds to metals through N as well as C? Give your argument by comparing it with CO. (5%)
5. Some hydrogen compounds may be unstable in water. (9%)
 (a) Write a balanced equation for each of the following by reacting with water: (6%)
 (i) CaH_2 (ii) CH_4 (iii) H_2S
 (b) Briefly describe the way they interact with water. (3%)
6. Make a unit cell drawing for the CsCl structure. Is it body-centered? Give your explanation. (4%)

類組：化學類 科目：無機化學(1003)

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7. On the complex ions: $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ (12%)

(a) Why they are of opposite charge? (2%)

(b) Draw the split 3d orbital for the central cobalt ion. (3%)

(c) Do both the complex ions exhibit same magnetic properties? Why? (2%)

(d) Which one is a high-spin case like $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$? And does it contain the same number of unpaired electrons as $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$? Why? (3%)

(e) Draw the crystal field diagram for the tetrahedral complex ion CoCl_4^{2-} . (2%)