1. The rate constants for the oxidation- reduction reactions are listed below.

$[Co(en)_3]^{3+} + Cr(H_2O)_6^{2+} \rightarrow$ 2×10^{-5} $(M^{-1}s^{-1})$

$[Co(NH_3)_6]^{3+} + Cr(H_2O)_6^{2+} \rightarrow$ 8.9×10^{-5}

$[Co(NH_3)_5Cl]^{2+} + Cr(H_2O)_6^{2+} \rightarrow$ 6×10^{5}

$[Co(NH_3)_5I]^{2+} + Cr(H_2O)_6^{2+} \rightarrow$ 3×10^{6}

(a) Which of these reactions proceed via outer-sphere mechanism and which via inner-sphere mechanism? (2%)

(b) For the reactions via inner-sphere mechanism, propose a reasonable mechanism and predict the final products. (3%)

2. The half life of water exchange are

$M(H_2O)_6^{2+} + {}^*H_2O \rightarrow M(H_2O)_5({}^*H_2O)$

$M = V^{2+}$ 10^{-2} sec

$M = Cr^{2+}$ 10^{-6} sec

(a) How many d-electrons in $V(H_2O)_6^{2+}$ and $Cr(H_2O)_6^{2+}$? (2%)

(b) Based on ligand field theory, explain why the rate of water exchange reaction for $Cr(H_2O)_6^{2+}$ is much faster than $V(H_2O)_6^{2+}$. (3%)

3. Based on 18-electron rule, predict the metal-metal bond order of the following organometallic compounds.

(a) $[CpMo(CO)_2]_2$ $Cp = C_5H_5$

(b) $[CpMo(CO)_2]_2^{2-}$

(c) $[CpFe(CO)_2]_2$ (5%)

4. What are the metals of the following bioinorganic compounds?

(a) chlorophyll (b) hemoglobin

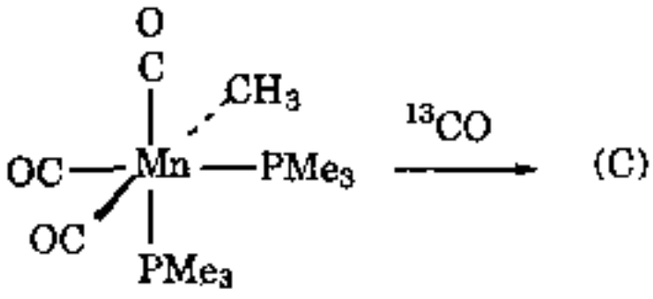
(c) coenzyme B_{12} (d) cytochrome P-450

(e) nitrogenase (5%)

5. Predict the products of the following reactions. (5%)

(a) $Mn(CO)_5^- + CH_2=CHCH_2Cl \rightarrow$ initial product (A)

$\xrightarrow{-CO}$ final product (B)

(b) 

(c) $Co_2(CO)_8 + H_2 \rightarrow$ (D)

(d) $[CpFe(CO)_2]_2 \xrightarrow{Na/Hg}$ (E)

6. When I_2 is dissolved in hexane and EtOH, the absortion wavelength of I_2 is quite different for these two solvents in the visible region (400-700 nm); this band is not due to charge transfer band. Explain the nature of this absorption band in details. In this visible light region, which solvent will show a higher absorption frequency for I_2? why ? (6%).

7. Show the number of d-d transition bands for the following high spin complexes in terms of term symbols. Ignore the Jahn-Teller distortion for the octahedral geometry. (8%)
(a) CrF_6^{3-} (b) $Co(H_2O)_6^{2+}$ (c) NiF_4^{2-} (d) CuF_4^{2-}

8. The effect of π- donor ligands such as X^- (X = F, Cl, Br and I) and π-acceptor ligands like CO, NO^+ will determine the 10 Dq values of the octahedron geometry. Draw the enengy diagram to show the effects of these two types of ligands. Which type of ligand will give a larger Dq value? (6%)

9. Briefly answer the following question and give your reason. (5%)
   (a) Choose the one that shows the strongest Jahn-Teller distortion.
   CrF_6^{3-}, MnF_6^{3-} (high spin), CoF_6^{3-}, $Ti(H_2O)_6^{3+}$, $Co(CN)_6^{3-}$

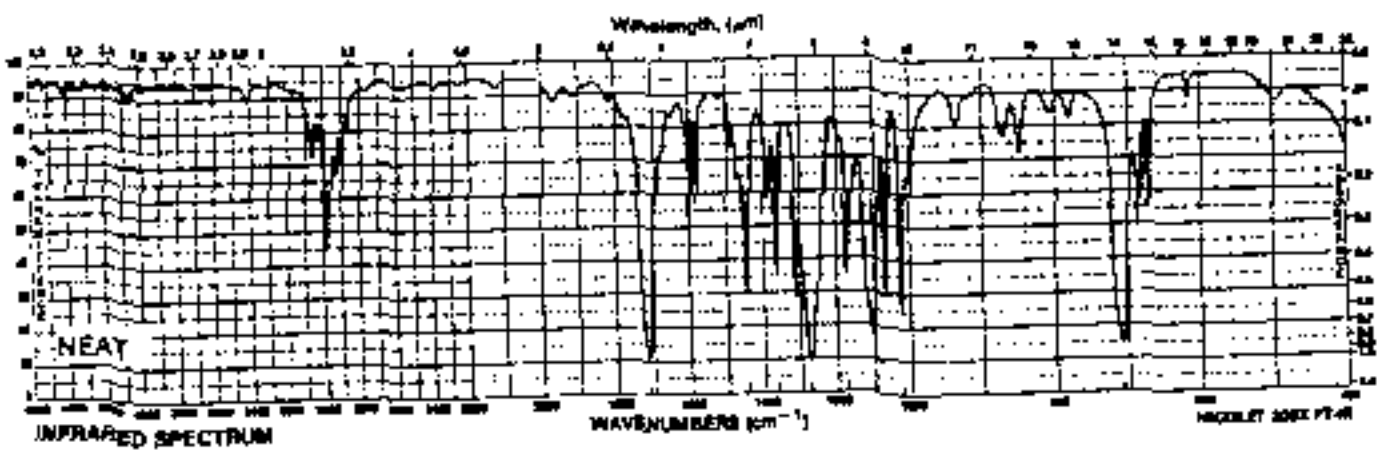
   (b) Compare the acidity of the following complexes in the increasing order
   BF_3, BCl_3 and BBr_3.

10. The Birch reduction provides a convenient method for making a product **A**, C_6H_8, from a compound **B**. The noise-decoupled ^{13}C NMR spectrum of **A** shows just two singlets, and the off-resonance decoupled spectrum of **A** shows only a triplet and a doublet.
   (a) Propose the structures of the reduced product **A** and the starting material **B**.
   (b) What reagents or conditions can be used for this reduction?
   (6%)

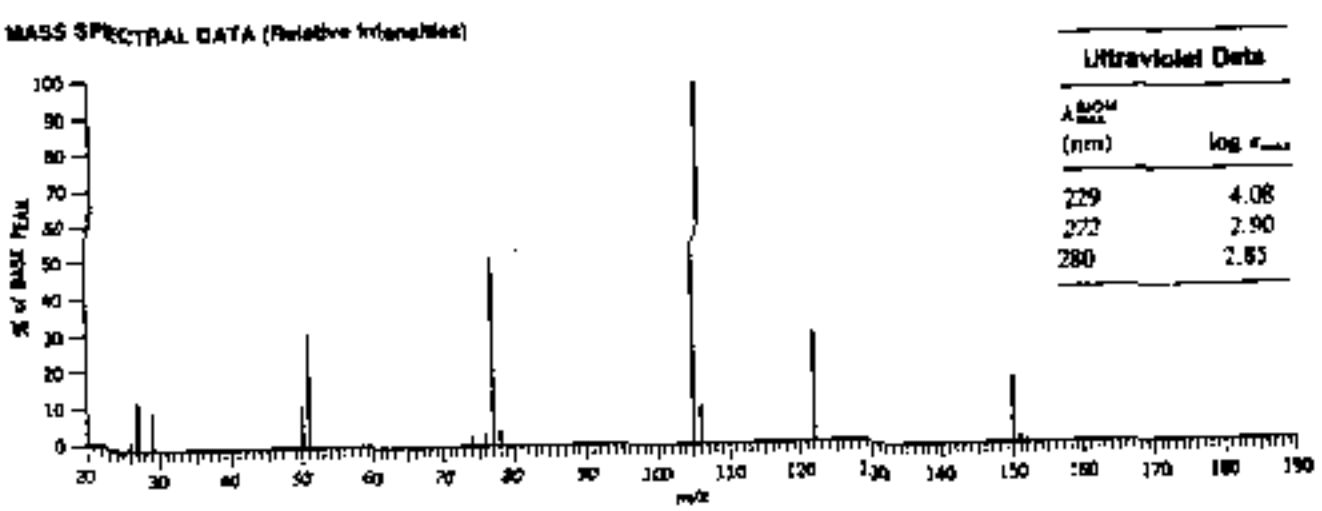
11. Compound **X** ($C_4H_8O_4$) gives a positive test with Tollen's reagent. Treatment of **X** with bromine water produces an optically active compound **Y**. Oxidation of **X** with nitric acid gives an optically inactive compound **Z**. Compound **X** can be prepared from D-glyceraldehyde by a Kiliani-Fischer synthesis. What are the structures of **X**, **Y**, and **Z**?
   (6%)

12. Give suitable answer for each of the following questions. (6%)
   (a) What product is formed in the crossed Claisen condensation between methyl benzoate and cyclohexanone?
   (b) Draw an acetic acid dimer. Be sure to indicate the hydrogen bonds present.
   (c) Provide the structure of the hydrate of cyclopentanone.
   (d) Provide an acceptable structure for spiro[4.4]nonane.
   (e) What is the hybridization of the central carbon of allene?
   (f) Why can't *N*-methyl-2-propanamine be resolved into isolable enantiomers even though the compound is chiral?

13. An unknown compound has the following set of spectral data. Deduce the structure and give *reasons for your* assignment. (8%)



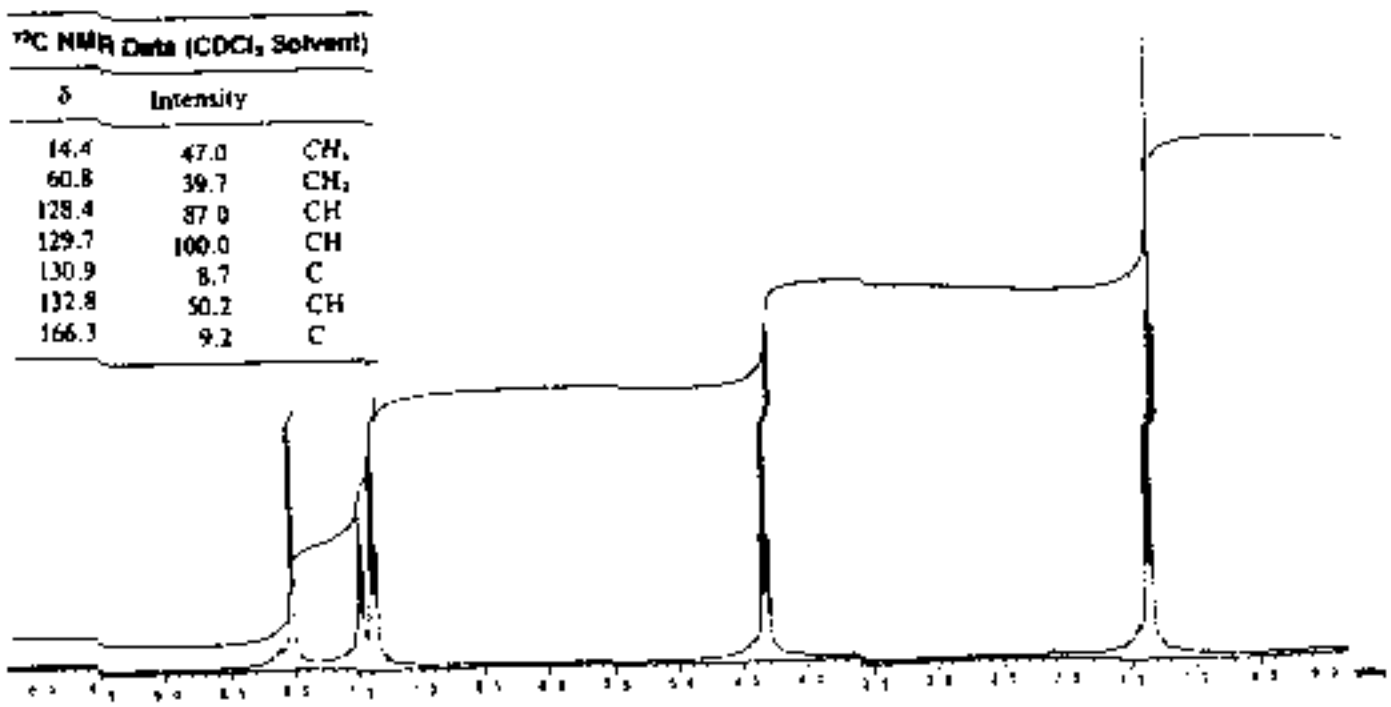
MASS SPECTRAL DATA (Relative Intensities)



Ultraviolet Data

λ_{max}^{EtOH} (nm)	$\log \varepsilon_{max}$
229	4.08
272	2.90
280	2.85

^{1}H NMR SPECTRUM (Solvent $CDCl_3$, 300 MHz)



^{13}C NMR Data ($CDCl_3$ Solvent)

δ	Intensity	
14.4	47.0	CH_3
60.8	39.7	CH_2
128.4	87.0	CH
129.7	100.0	CH
130.9	8.7	C
132.8	50.2	CH
166.3	9.2	C

選擇題 (3% for each)

14. The Robinson annulation reaction includes
    (a) Diels-Alder reaction followed by Claisen rearrangement
    (b) Wittig condensation followed by Grob fragmentation
    (c) Michael addition followed by aldol condensation
    (d) Birch reduction followed by dehydration

15. Which of the following reaction involves a radical intermediate:
    (a) Bayer-Villiger reaction
    (b) Barton reaction
    (c) Peterson olefination
    (d) Dieckmann condensation

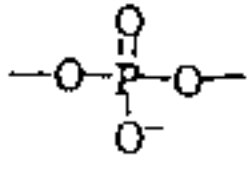
16. Which of the following species is considered as a hard acid:
    (a) Al^{3+} (b) Cu^{+} (c) $C_6H_5^{+}$ (d) BH_3

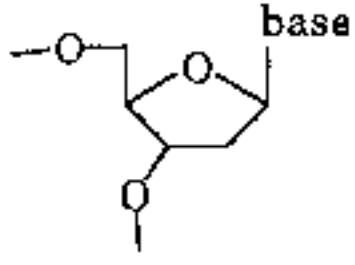
17. The correct order of bond energies is:
    (a) O–H > H–Cl > Si–F
    (b) Si–O > C–S > O–O
    (c) C–H > N–N > C–C
    (d) S–S > N–H > C–Cl

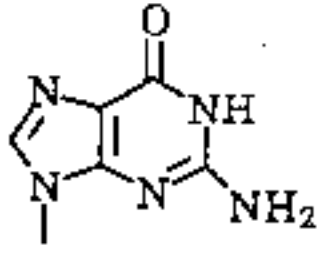
18. Which of the following compounds is given a correct pKa value relative to water (pKa = 15.7)
    (a) 20 for CH_4
    (b) 30 for EtOH
    (c) 35 for PhSH
    (d) 34 for NH_3

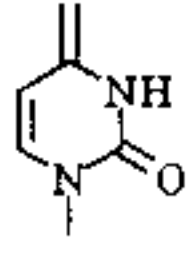
19. Which of the following reagent can oxidize a cycloalkanone to a lactone:
    (a) CrO_3 (b) *m*-CPBA (c) $KMnO_4$ (d) SeO_2

20. Deoxyribonucleic acid does not contain

(a) 

(b) 

(c) 

(d) 

21. Which of the following compounds does not belong to heterocyclic compounds

(a) aniline (b) pyrrole (c) furan (d) thiophene