OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree (Chemistry) Examination Part III
CHM 307: APPLICATION OF SPECTROSCOPIC TECHNIQUES
Harmattan Semester Examination (2022/2023 Session)

Date: 4th March 2024 **Time allowed: 2½ hrs**

Instruction: Attempt any one question in Section A and ALL questions in Section B

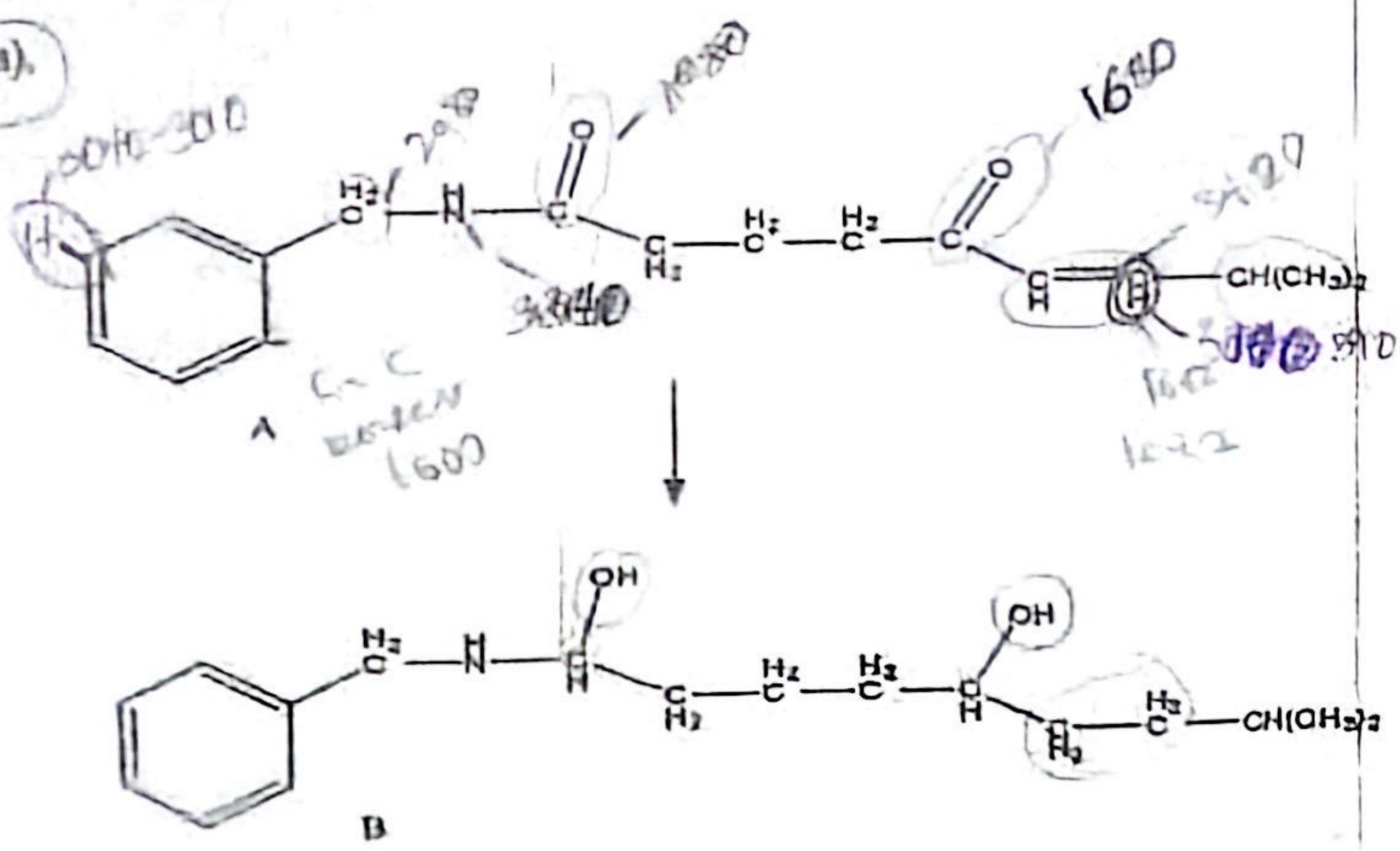
SECTION A

Question 1 (15 marks)

1. Differentiate between the following compounds using the spectroscopic method(s) indicated:
   - (i) Cyclohexanone and 2-cyclohexenal (α,β-unsaturated cyclohexenal) - IR & UV - 6mks
   - (ii) Butanamide; *N*-methylpropanamide and *N,N*-dimethylethanamide - IR only
   - (iii) 1,1,3-trichloro-4,6-dimethylhepta-1,3,5-trien and 1,1,3-trichloro-1,4,6-dimethylhepta-4,6-trien - UV only

Question 2 (15 marks)

2 (a).



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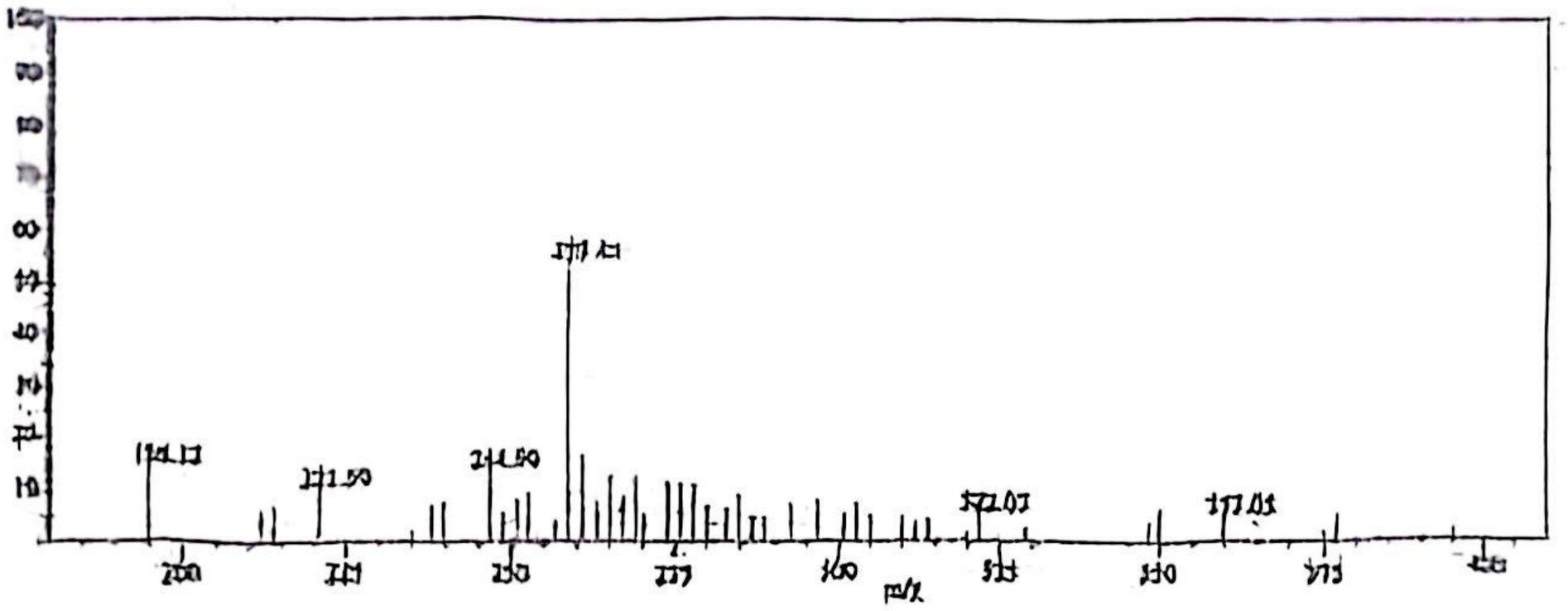


Figure 5: Mass spectrum of zinc (II) complex.

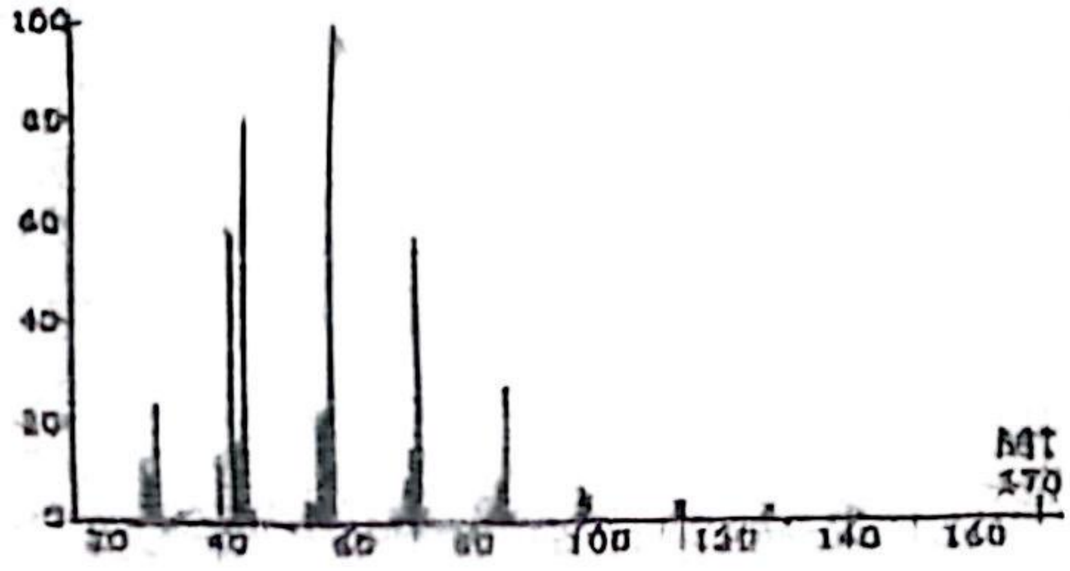
Question 6 (20 marks)

(a) Mention two of the striking diagnostic features of aliphatic alcohols.

(b) Below is a mass spectrum of one of the prominent compounds that are commonly found in crude oil.

(i) Interpret the spectrum and determine the structure and name of the compound.

(ii) Show the mechanism of fragmentation that resulted in the following ions m/z 43, 57, 85 and 99.

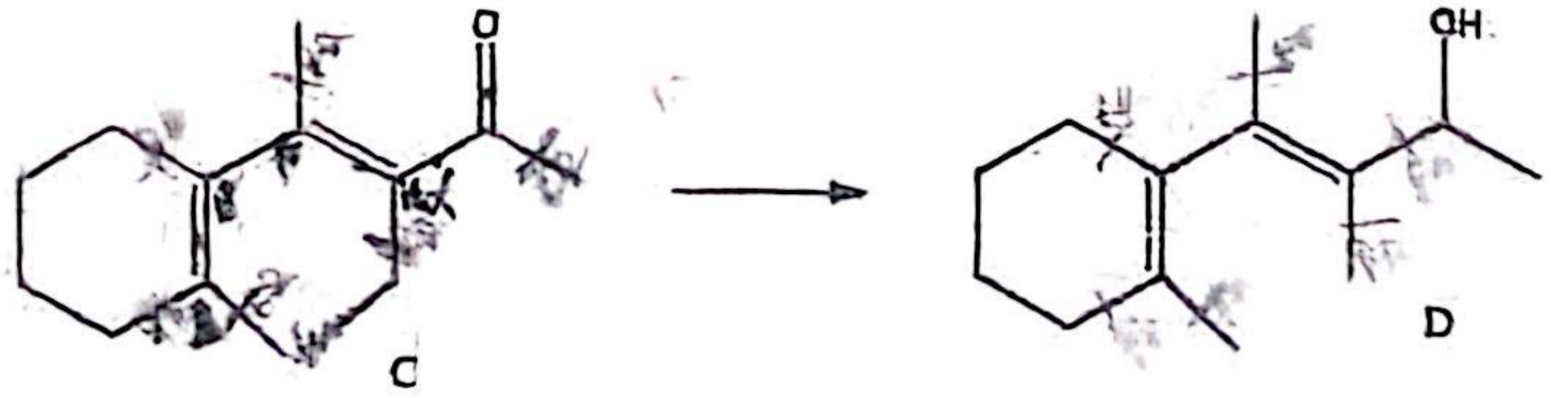


The spectrum of compound A shows significant absorption at the following IR frequencies: 3420, 3050, 2980, 1700, 1670, 1642 1600 cm^{-1}.

(i) Which specific functional groups in compound A are most likely responsible for these absorptions?

(ii) If compound A is converted to B, which of the listed absorptions would disappear and which new absorption(s) would show up?

(b)



Consider the transformation of compound **C** to **D** above:

(i) Deduce the UV (λ_{max}) values for **C** and **D**; hence

(ii) How do you describe the transformation of **C** to **D** in UV terms?

SECTION B. ATTEMPT ALL QUESTIONS IN THIS SECTION

Question 3 (15 marks)

3a. The ^1H NMR spectrum of a synthetic organic compound **E** with molecular formula $C_7H_{14}O$ has three kinds of hydrogens. The ratio of the integration area of each kind of protons is 1.50, 2.30 and 6.80.

(i) Determine the integral height per hydrogen in the molecule

(ii) Calculate the number of each kind of hydrogens in the molecule and deduce the structural features which corresponds to the number of each kind of hydrogens in compound **E**

(iii) If each kind of hydrogens appears as a singlet in the spectrum, propose a structure that is consistent with the structural features in (ii)

3b. The ^1H NMR spectral of some synthetic organic compounds have the following features:

(I) Multiplicity of signals

(II) Chemical shift value for each type of protons

(III) Signals

(IV) Integration area

Give one specific information that can be obtained from each of these features

3c. Comment briefly on the chemical shifts in the ^{1}H-NMR of the following compounds:

(i) H_3CCl δ 3.10 ppm

(ii) H_2CCl_2 δ 5.30 ppm

(iii) $HCCl_3$ δ 7.30 ppm

(iv) H_3CCH_3 δ 0.90 ppm

Question 4 (10 marks)

4a. A synthetic organic compound X has a molecular formula of $C_4H_8O_2$. It exhibited two strong IR absorption bands at V_{max} 2840 and 1735 cm^{-1}. The ^{1}H NMR signals (ppm) appeared at δ:

(i) 4.13 (2H, q, J = 4.5 Hz)

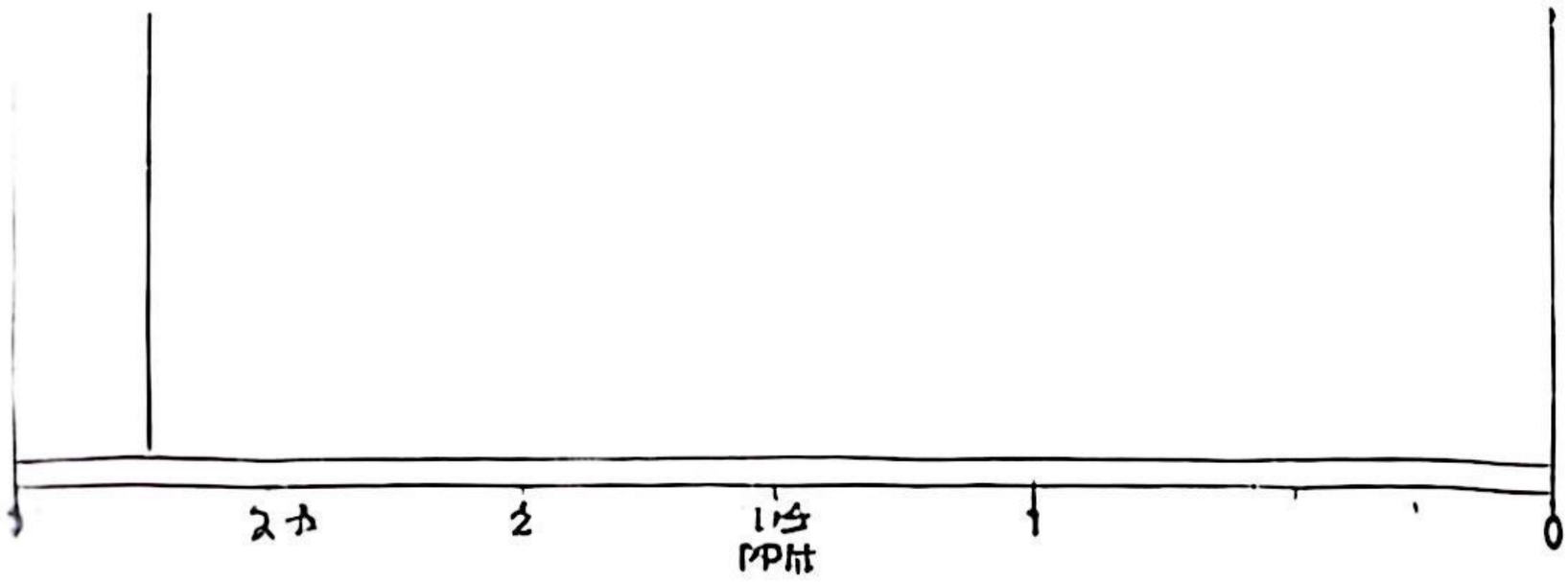
(ii) 2.21 (3H, s)

(iii) 1.29 (3H, t, J = 4.5 Hz)

Deduce the structural features which you would expect in the molecule and postulate a structure which you consider as being most consistent with the given spectroscopic data.

4b. A secondary metabolite Y isolated from a Nigerian medicinal plant was analysed to have molecular formula of $C_6H_8O_2$. The molecule exhibited two strong IR absorption bands at V_{max} 2930 and 1705 cm^{-1}. The ^{1}H NMR spectrum of compound Y is presented below. Assign the spectroscopic data appropriately and deduce the possible structure of compound Y.

^{1}H NMR Spectrum of Compound Y



Question 5 (20 marks)

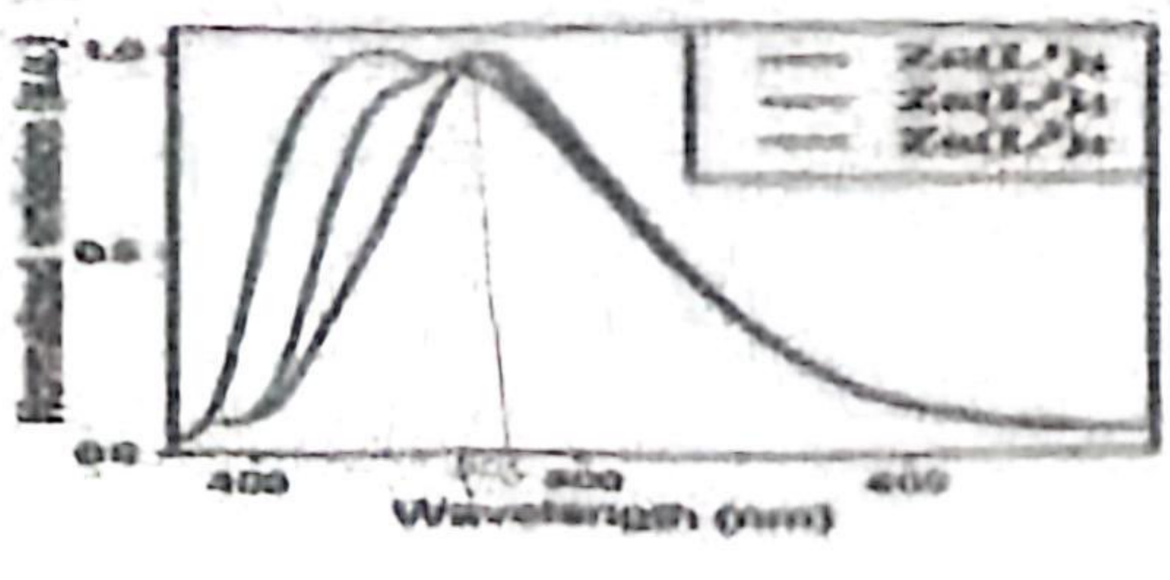


Figure 1: UV-Visible spectra of zinc (II) complexes.

5a. The electronic spectra above (Fig. 1) belong to zinc (II) complexes.

i. What is the origin of these bands?

ii. Explain your answer in 5a (i), above.

5b. The two compounds drawn below (Fig. 2), exhibit linkage isomerism. The yellow isomer is named pentaamminenitrito-N-cobalt (III) ion and red isomer is pentaamminenitrito-O-cobalt (III) ion. How would you use infrared spectroscopy to distinguish between the two isomers?

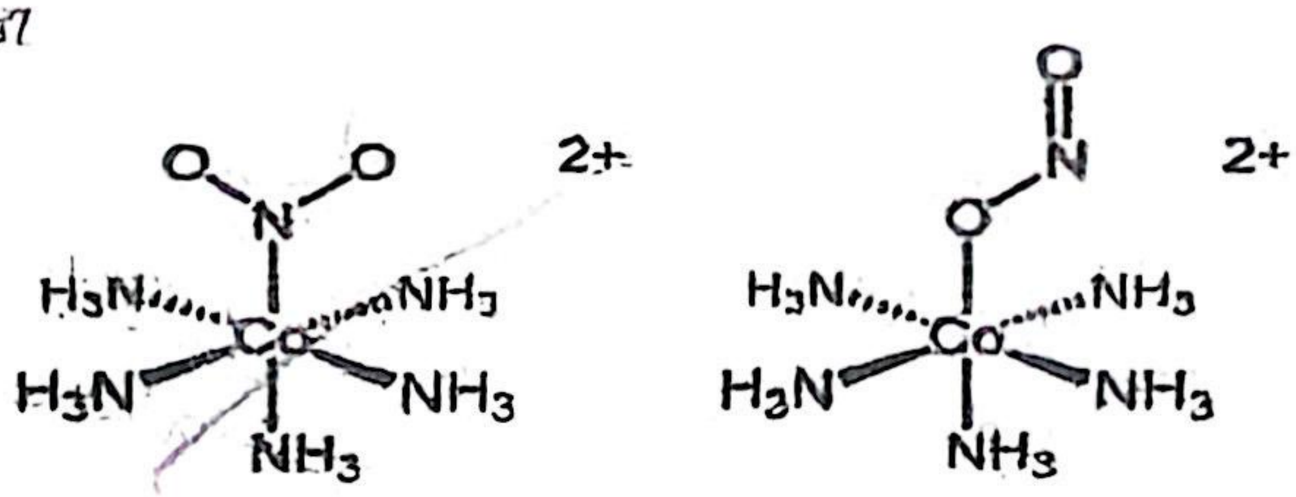


Figure 2: Cobalt (II) complexes displaying linkage isomerism.

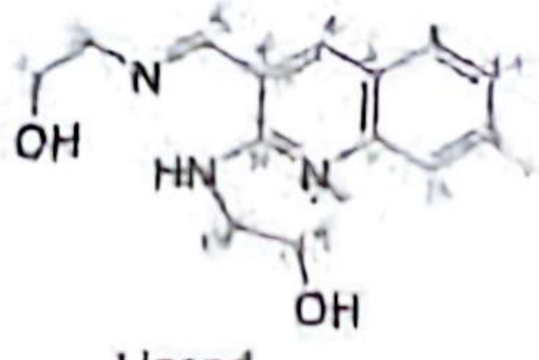
5c. The diagrams of the structure of ligand and its zinc (II) complex are given in (Fig. 3) below. The Infrared spectra of the ligand and its zinc (II) complex is given in Fig. 4A and B respectively, while Fig. 5 is the mass spectrum of the zinc (II) complex.

i. What are the functional groups where the binding of the ligand to zinc (II) occurs?

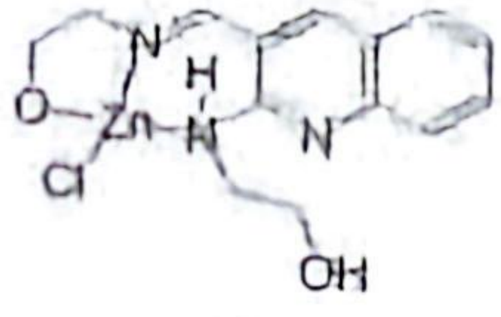
ii. Interpret the IR spectra to elucidate the formation of the complex.

iii. In the mass spectrum, account for the molecular ion peak and the m/z peak at 332.07. [O = 16, N = 14, C = 12, H = 1, Cl = 35.5, Zn = 65.4]

iv. What structural orientation does the zinc (II) complex exhibit?

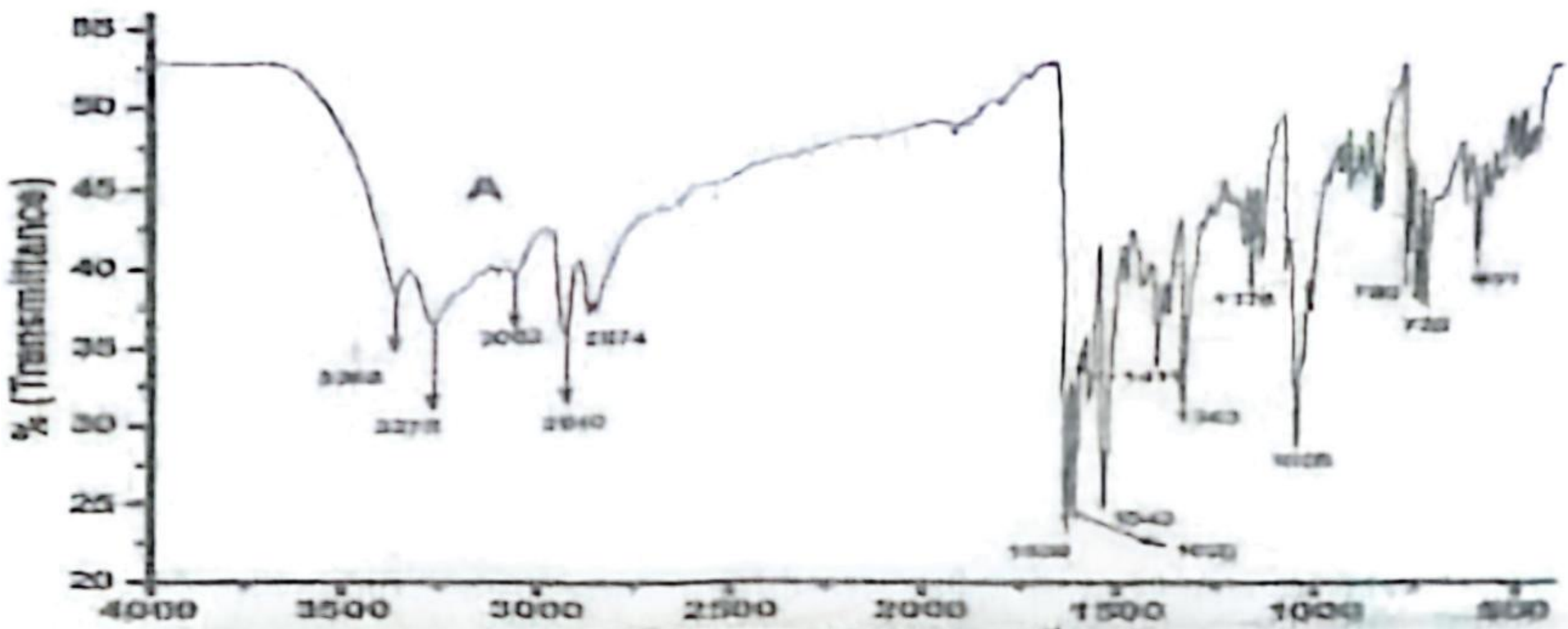


Ligand

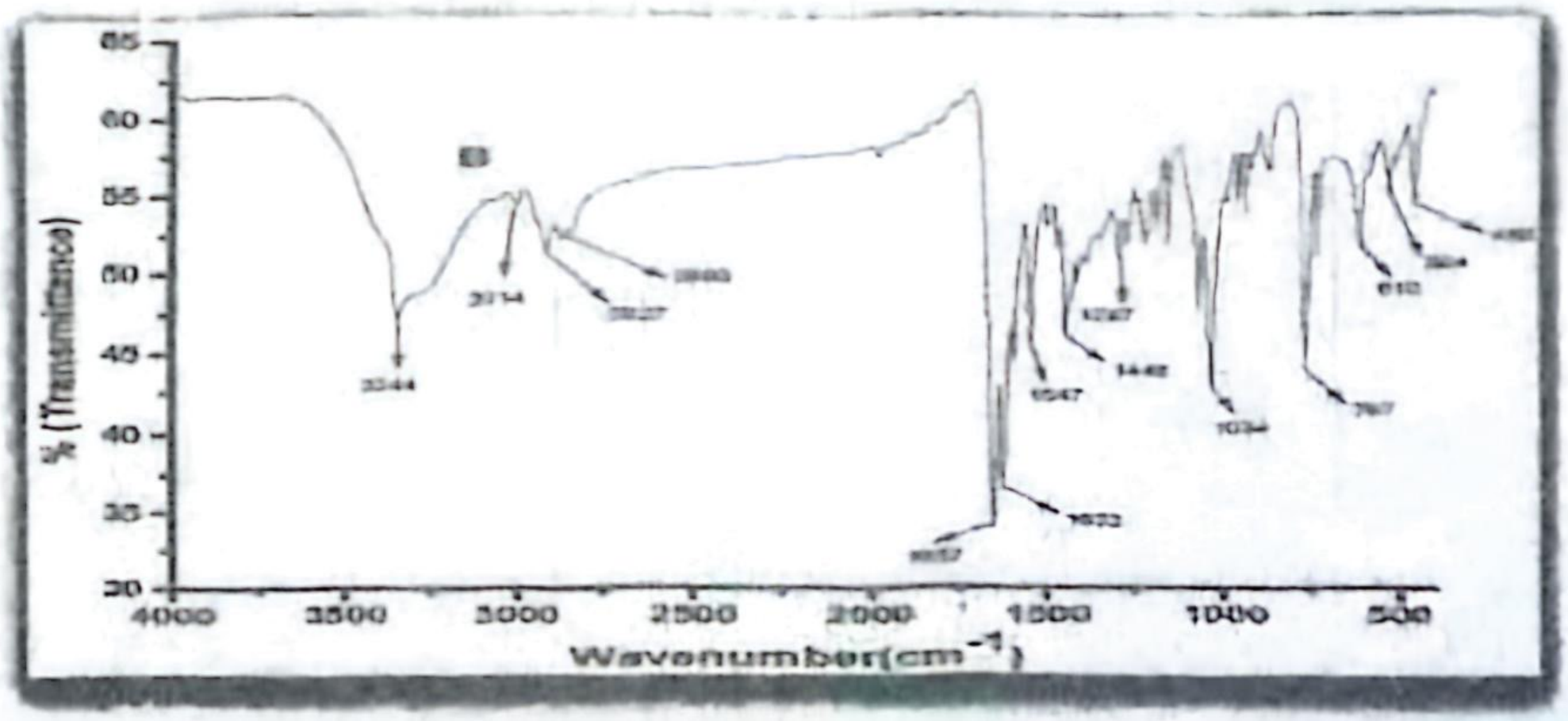


zinc(II) complex

Figure 3: Structure of ligand and Zinc (II) complex



(A): IR spectrum of ligand.



(B): IR spectrum of zinc (II) complex

Figure 4: A and B are the infrared spectrum of the ligand and zinc (II) complex.