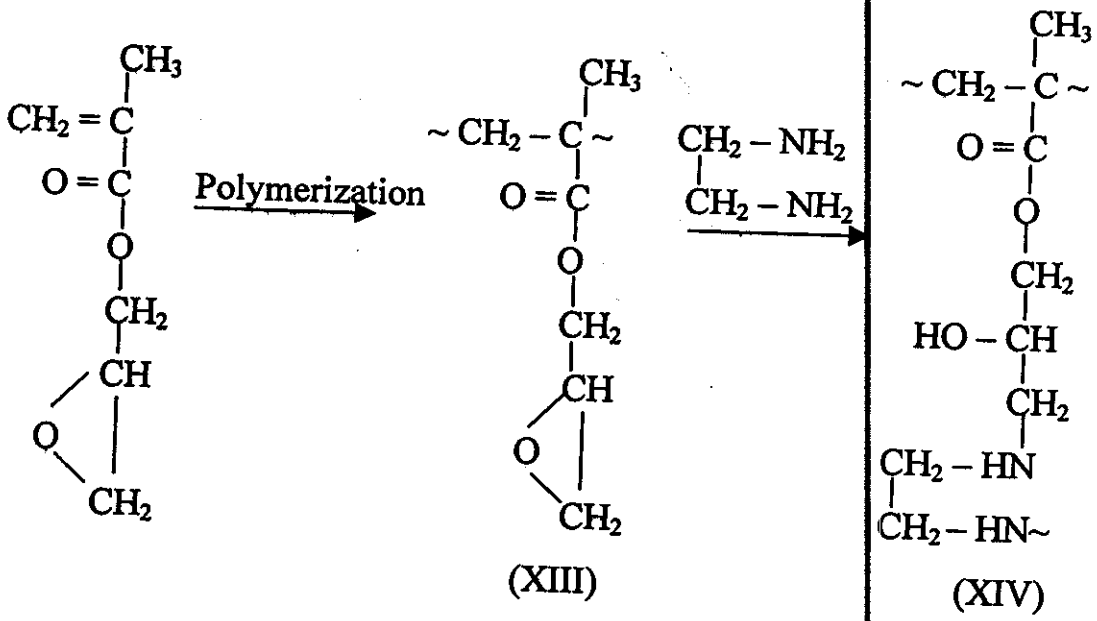
Results and Discussion

RESULTS AND DISCUSSION

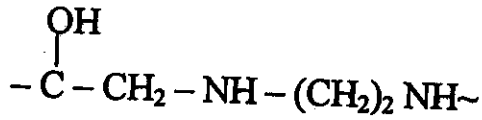
1) Metal complexes of poly (GMA bearing en) (XVII)

The ligand was obtained according to the following scheme



(XIII) (XIV)

The IR-spectrum of product(XIII) is given in Fig. (1a-b). The spectrum shows bands near 3442 (w), 3001-2851 (splitted), 1735 (s), 1265 (m) cm^{-1}. These bands are assigned to νOH of water, νCH-Aliph, νC=O and epoxide moiety, respectively. On treatment of (XIII) by ethylenediamine, the IR- spectrum of the product (XIV) displays a new band attributed to (en) near 3442 cm^{-1} with shoulder at 3250 cm^{-1}. These bands are assigned to νNH and confirming the opening of epoxy ring by amine to give



Moreover the spectrum of (XIV) is also characterized by the disappearance of the epoxide band at 1265 cm^{-1}, confirming the formation of (XIV). The metal complexes obtained are insoluble in all

common solvent. The IR spectra of the metal complexes obtained are characterized by the shift of νNH to lower frequency whilst the bands of both νC = O and νOH appear at the same positions of the ligand Fig. (1a-b). This behaviour indicate that the polymer coordinates only through the two nitrogen atoms of ethylenediamine moiety.

The solid electronic spectra of the metal complexes in nujol mulls display bands near 18827 (for Co^{2+}) 15552 (for Ni^{2+}) and 15708 cm^{-1} (for Cu^{2+}) Fig. (2a-c). The appearance of these bands confirm an octahedral geomtry around these metal ions [91].

Thermal analysis

The polymeric ligand and its metal complexes under investigation are characterized by a high content of water molecules. This can be obtained from the DTA and TG curves, Fig. (3a-b). The DTA curves of the complexes show an endothermic DTA peak in the temperature range 25-123°C. This peak is assigned to loss of hydrated water as indicated from the TG weight losses.

DTA and TG curves also show that the compounds are simultaneously decomposed after dehydration through endothermic events. The metal complexes show a higher thermal stability relative to that of the ligand. The TG weight losses data show that the ligand gives zero remaining weight, whereas the metal complexes give a reasonable percentage of remaining metal or metal oxides. This behaviour confirm the formation of metal complexes.

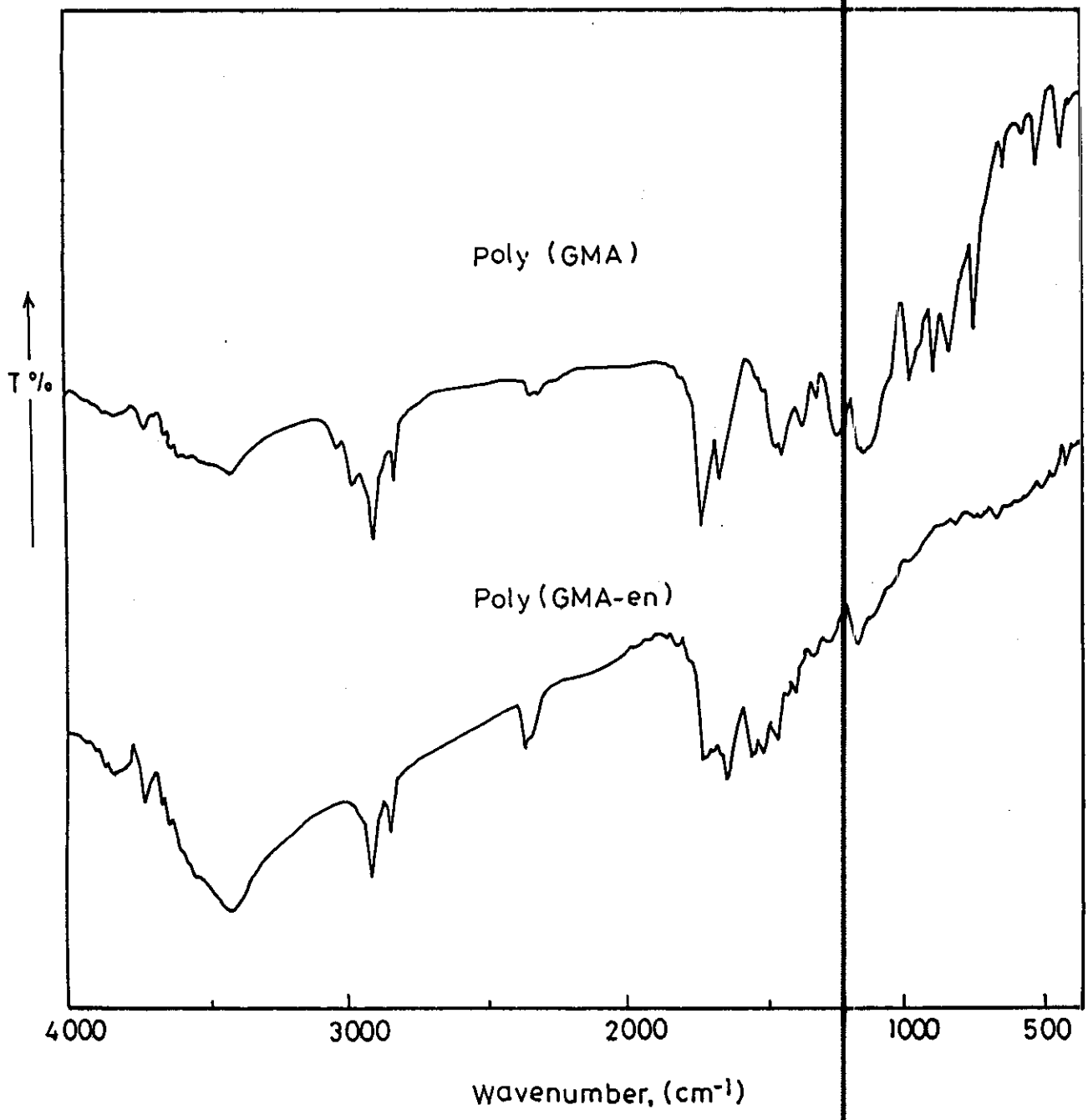


Fig. (1-a) : IR-Spectra of poly (GMA) (XIII) and poly (GMA bearing en) (XIV)

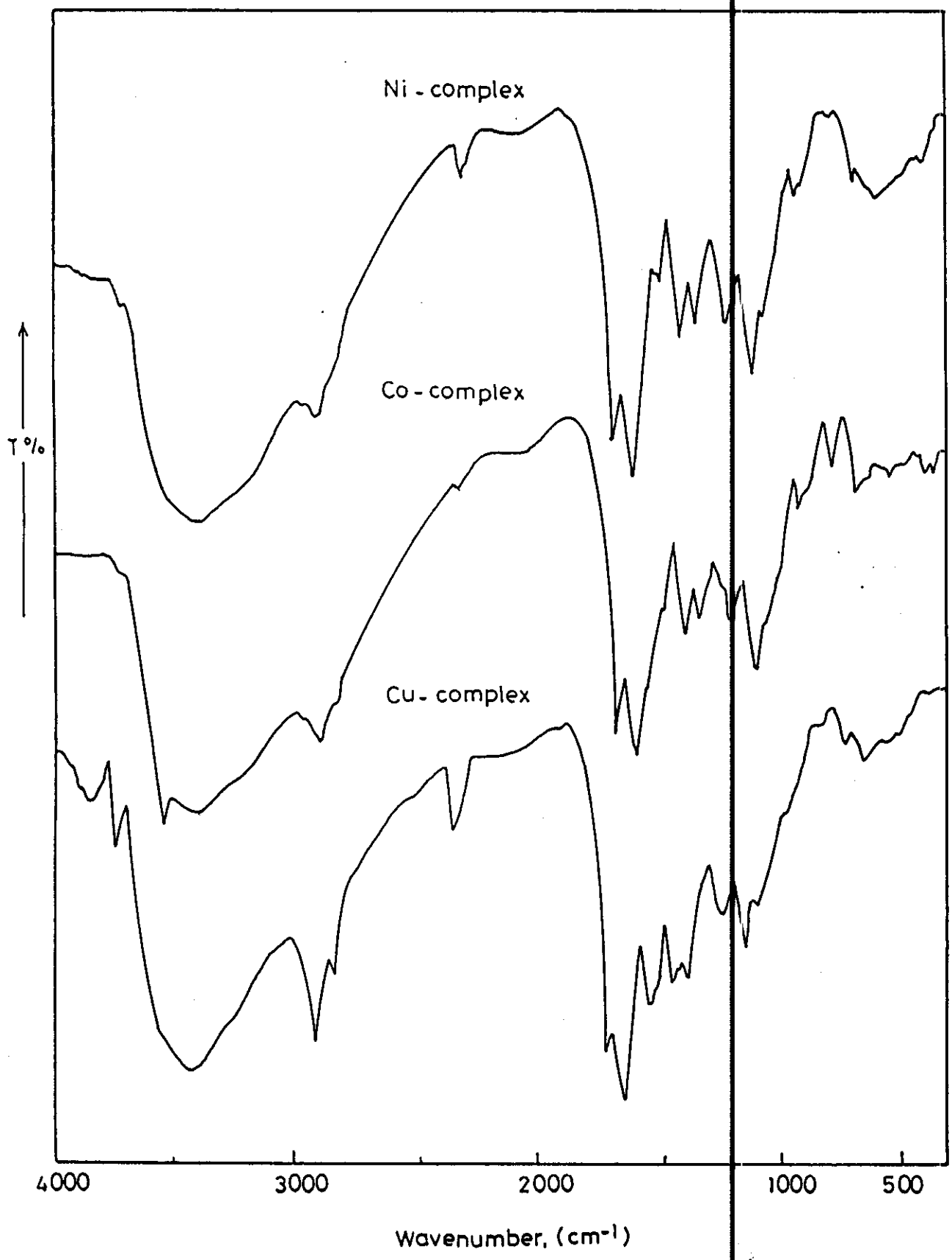


Fig. (1-b) : IR-Spectra of poly (GMA bearing en) metal complexes

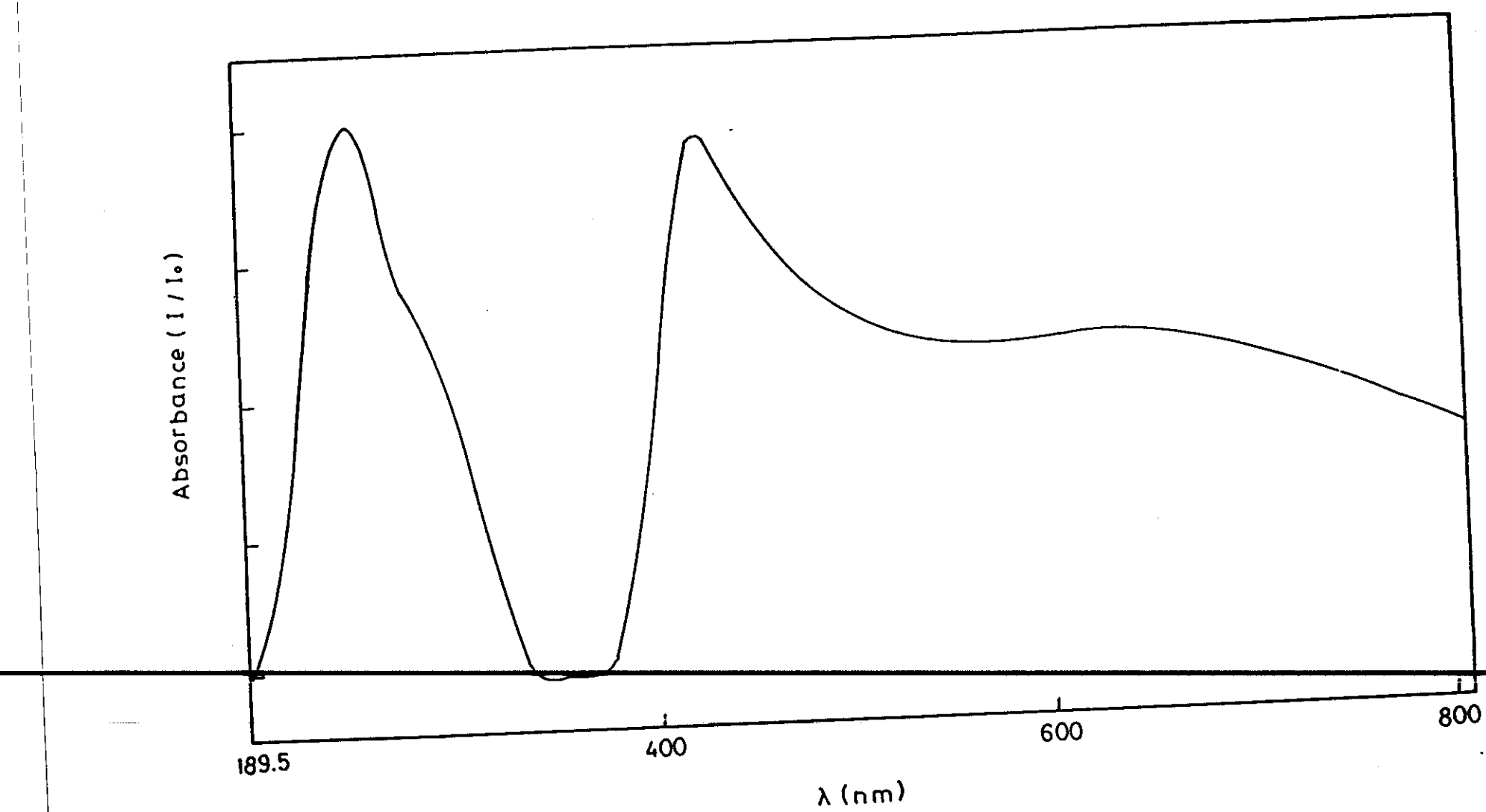


Fig. (2-a) : Electronic spectra of poly (GMA bearing en) Copper complex

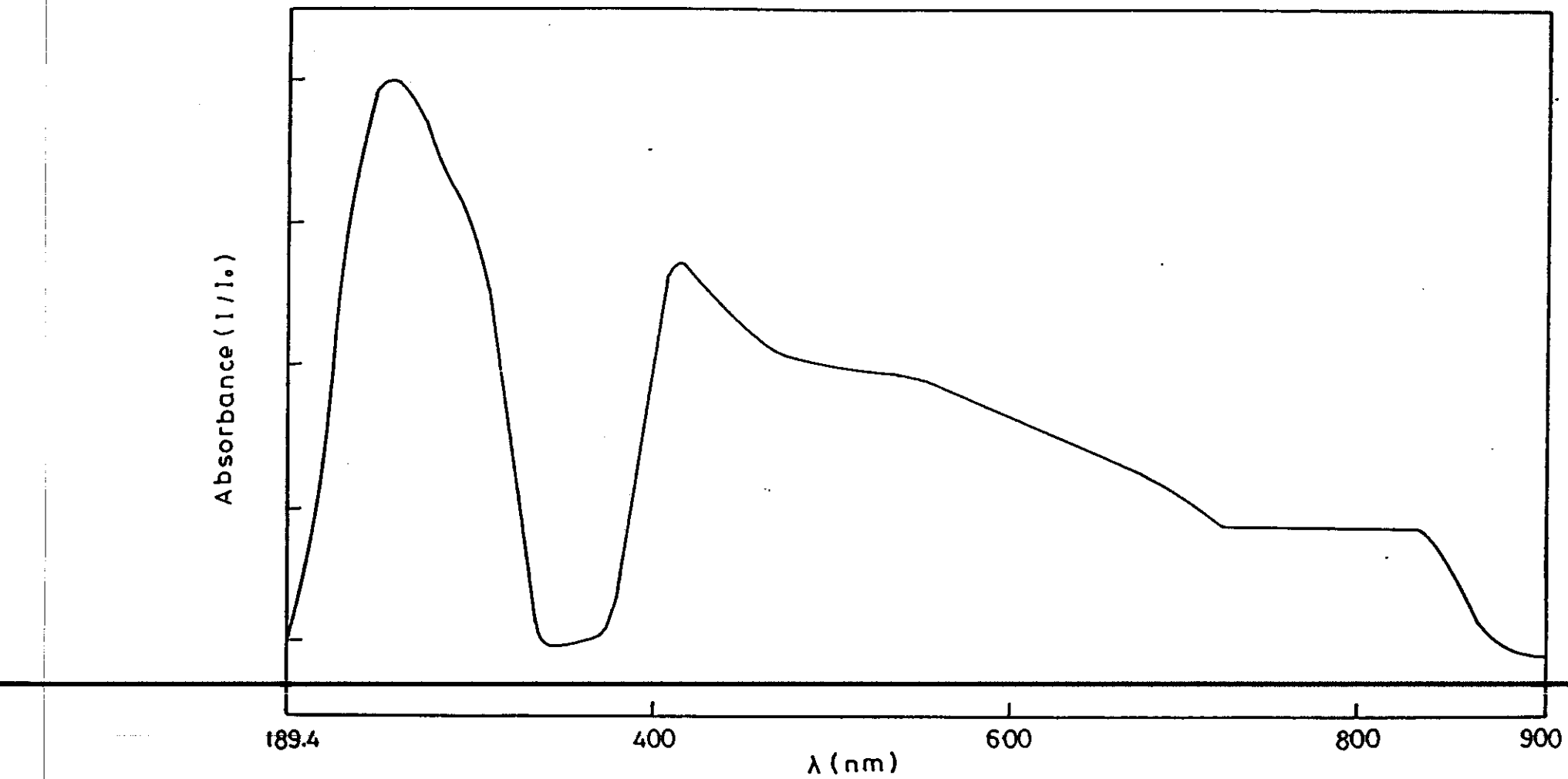


Fig. (2-b) : Electronic spectra of poly (GMA bearing en) Cobalt complex

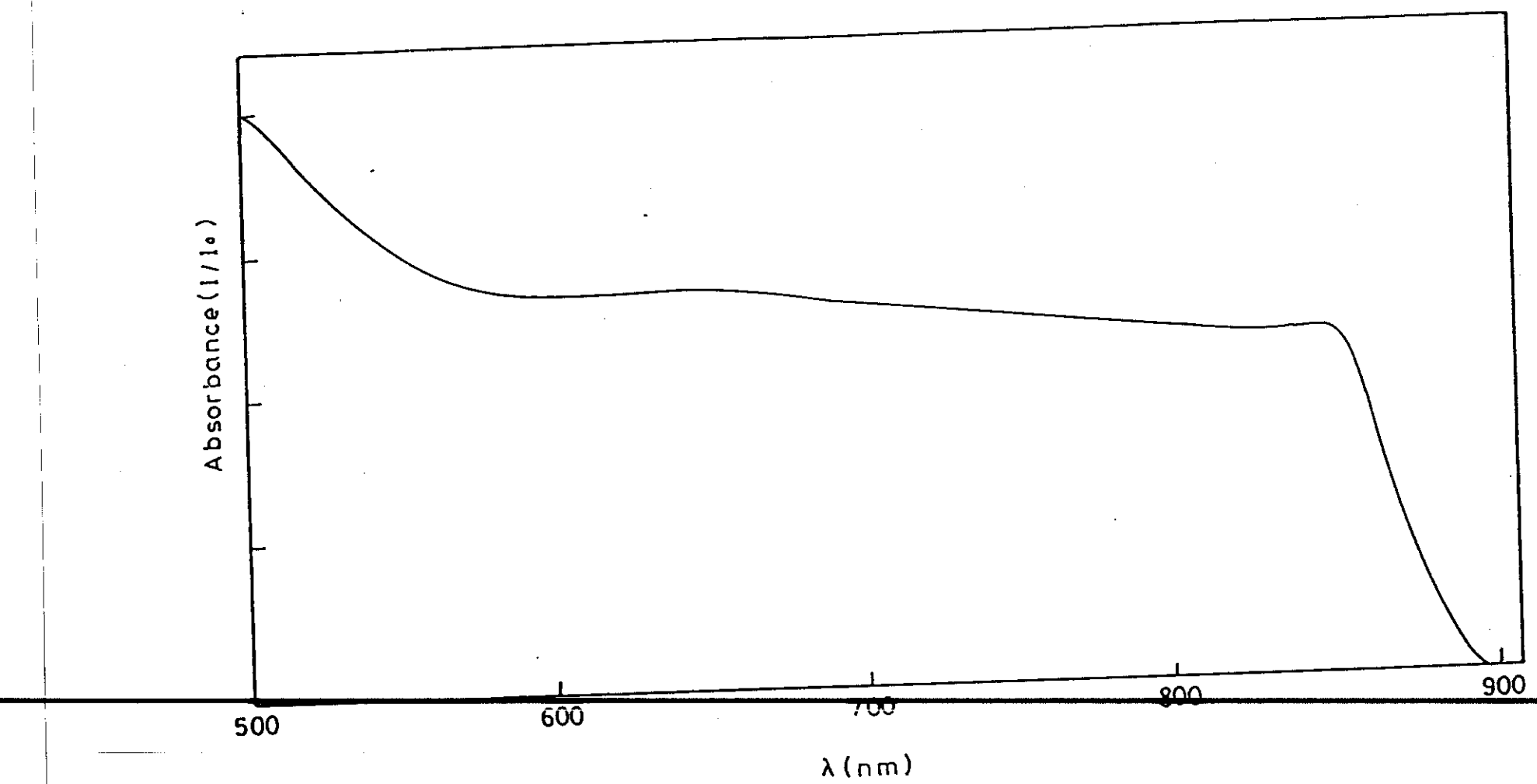


Fig. (2-c) : Electronic spectra of poly (GMA bearing en) Nickel complex

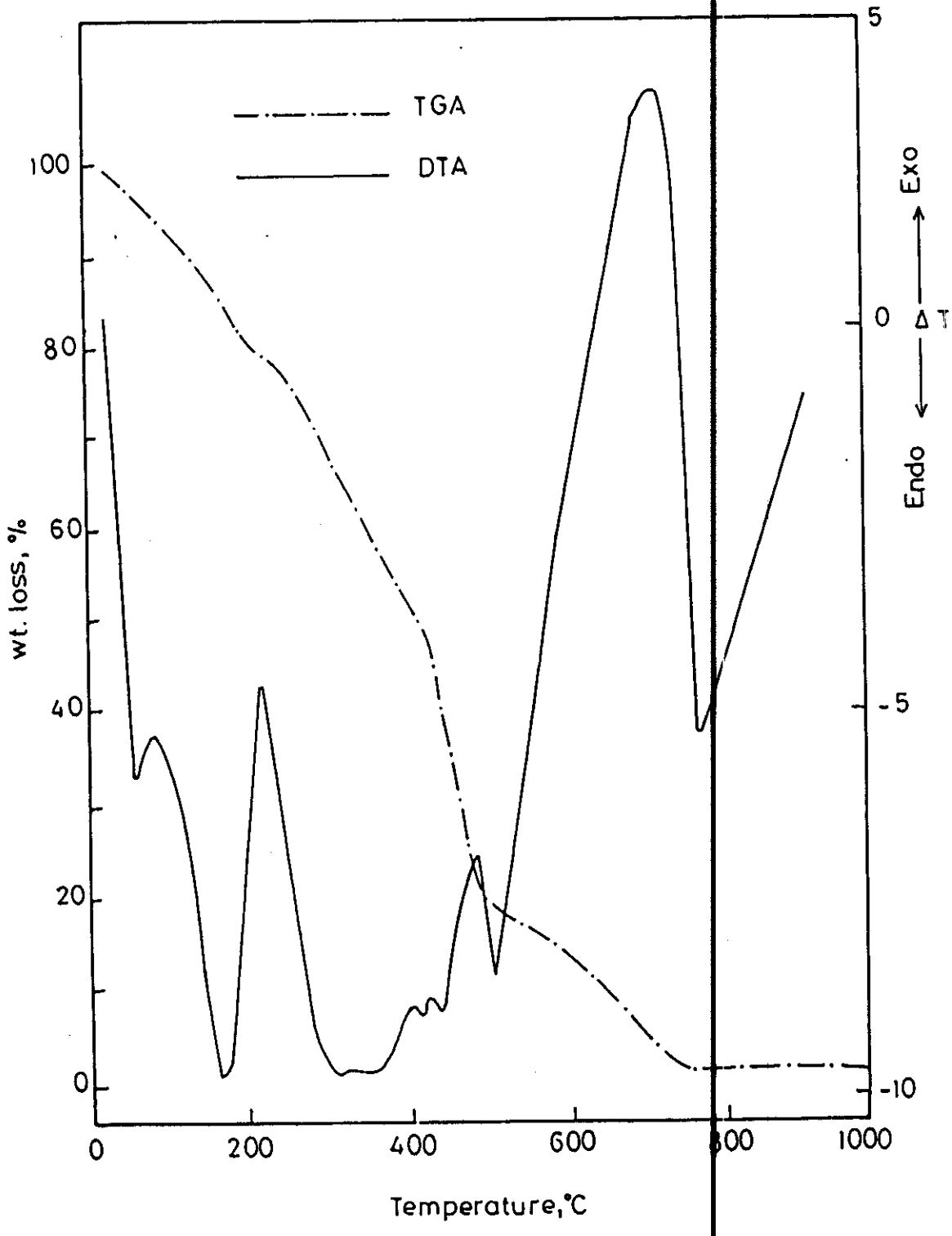


Fig. (3-a) : DTA and TGA curves of poly (GMA bearing en) (XIV)

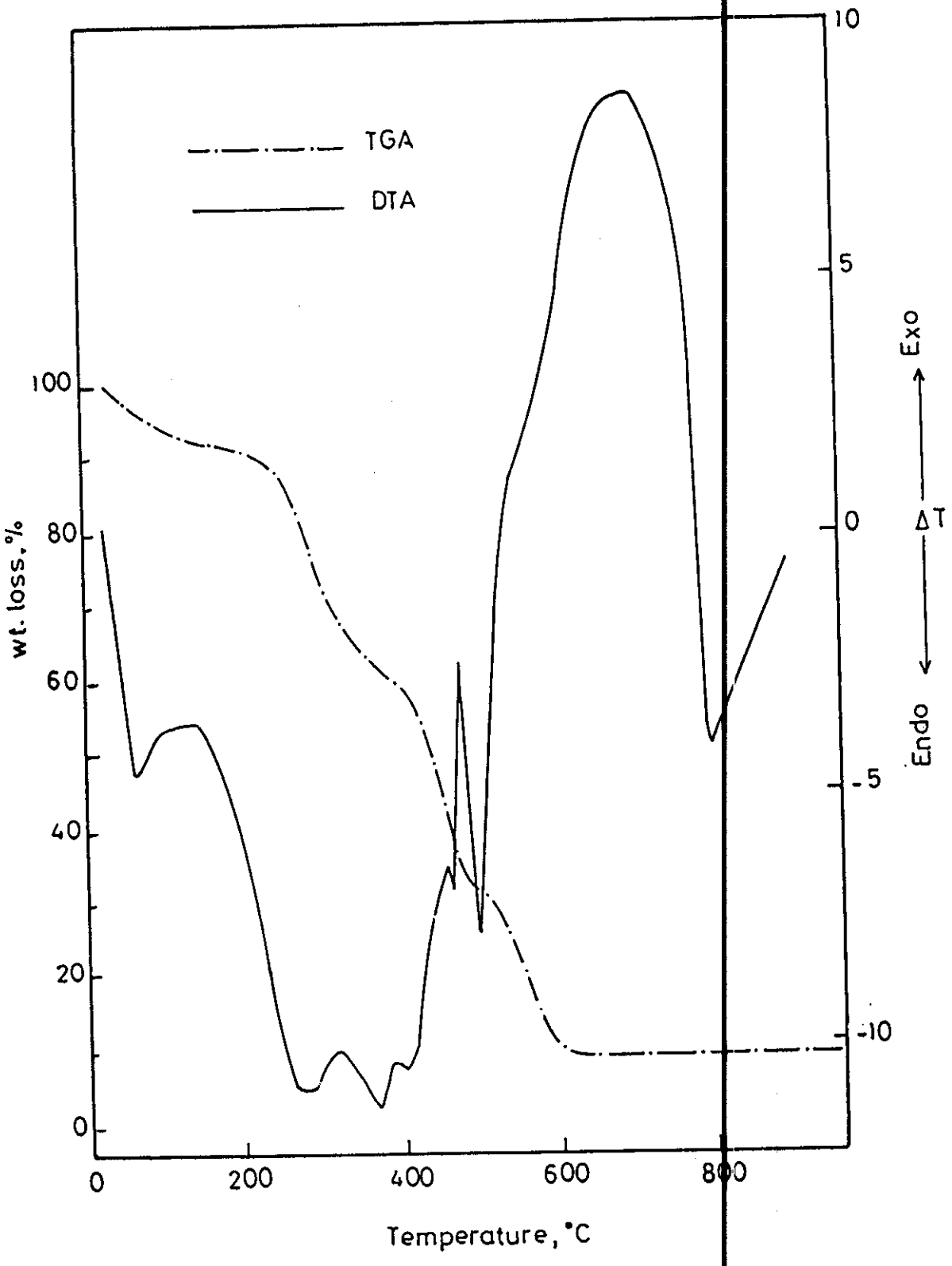


Fig. (3-b) : DTA and TGA curves of poly (GMA bearing en) copper complex

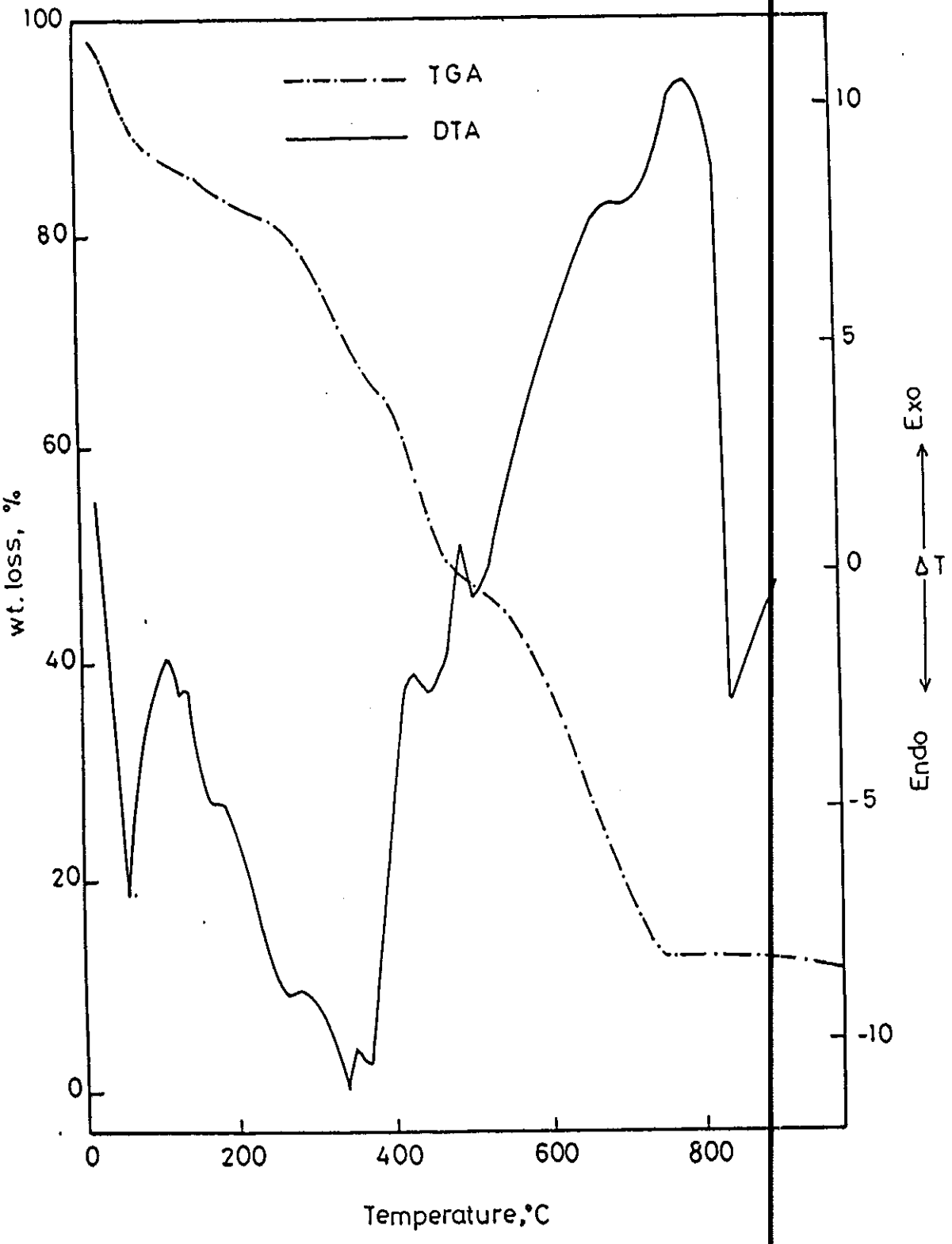


Fig. (3-c) : DTA and TGA curves of poly (GMA bearing en) cobalt complex

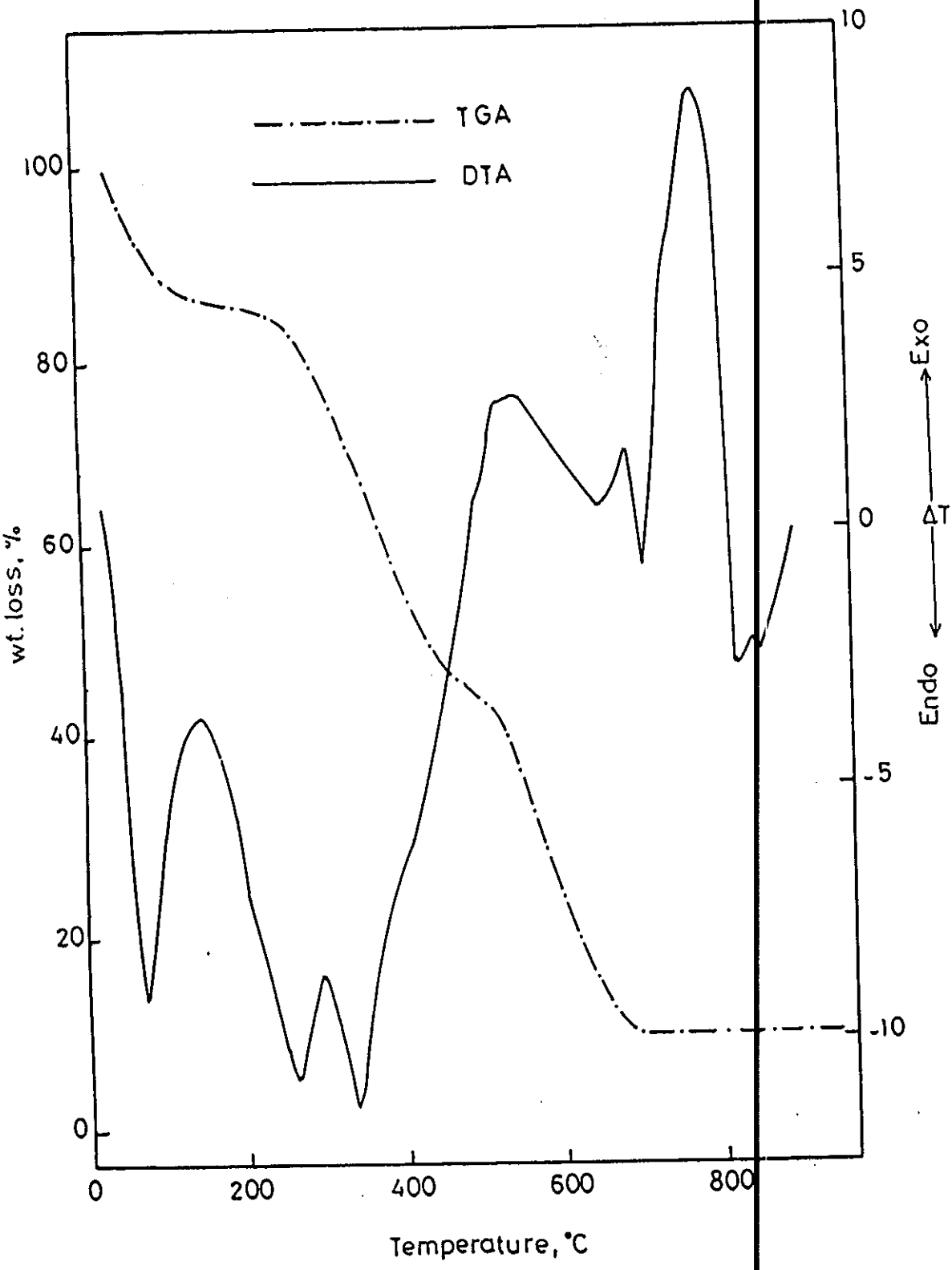


Fig. (3-d) : DTA and TGA curves of poly (GMA bearing en) nickel complex.

2) Metel complexes of poly (GMA bearing 4aapy) (XVIII)

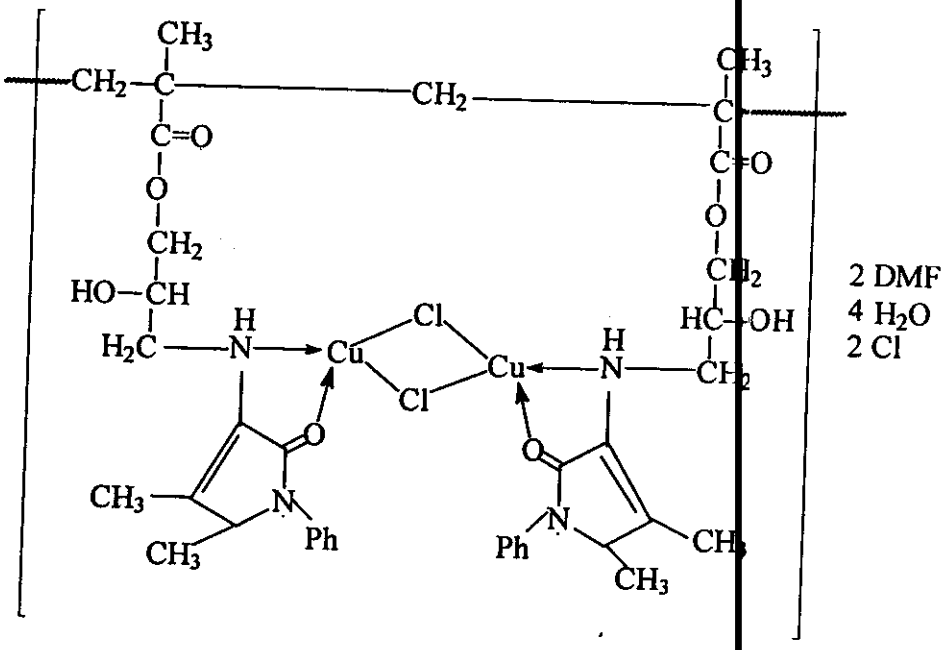
As indicated before the IR sepectra of poly-GMA (XIII) display bands near, 3004-2851 (splitted) 1735 (s), 1265(m) cm^{-1} Fig (4a-b). These bands are assigned to, νCH-Aliph, νC=O and epoxide moiety, respectively. On treatment with 4-Amino-antipyrine the polymer (XV) obtained displays new bands near 3400, 1650, 1380 and 1070 cm^{-1}. These bands are assigned to νNH/OH, νC=O[92] of pyrazolone ring, δ(C-OH)[22] and (C-N), respectively. This indicate the bearing of GMA polymer (XIII) by 4-Amino-antipyrine through the opening of the epoxy ring.

On reaction with copper (II) chloride, the spectrum of the metal complex obtained is dramatically changed from that of ligand in both the intensity and shape of the peaks Fig. (4a-b). Also the position of same peaks, especially δNH 3350cm^{-1}, νC=O 1560cm^{-1} of pyrazolone ring νC-N 1050cm^{-1} are shifted to lower frequency. Whilst the peaks of νC=O (1730 cm^{-1}) of ester, νOH (3400 cm^{-1}) and δ C-OH (1380 cm^{-1}) show no shift on complexation. This behaviour indicate that the chelating polymer obtained behaves as neutral bidentate lignad through nitrogen of (NH-group) and oxygen of the carbonyl group of pyrazolone ring. The spectrum display also a strong band at 1655 cm^{-1}. This band is assigned to νC=O of dimethylformamid (DMF) which included in the structure of complex as a solvent of crystallization.

The TG study gives a weight-loss (12.3 %) at 210 °C corresponding a loss of 1 molecule of DMF Fig. (5). The electronic spectrum of the complex in nujol mulls displays a band near 13800 cm^{-1}. This band is assigned to pseudotetrahedral distorted towards square planar[91].

The observed lower value of magnetic moment (1.31 BM) may be attributed to the copper-copper interaction in the di-chloro four-membered ring[93].

These data together with the elemental analysis table (1) suggest the following structure:



(XVIII)

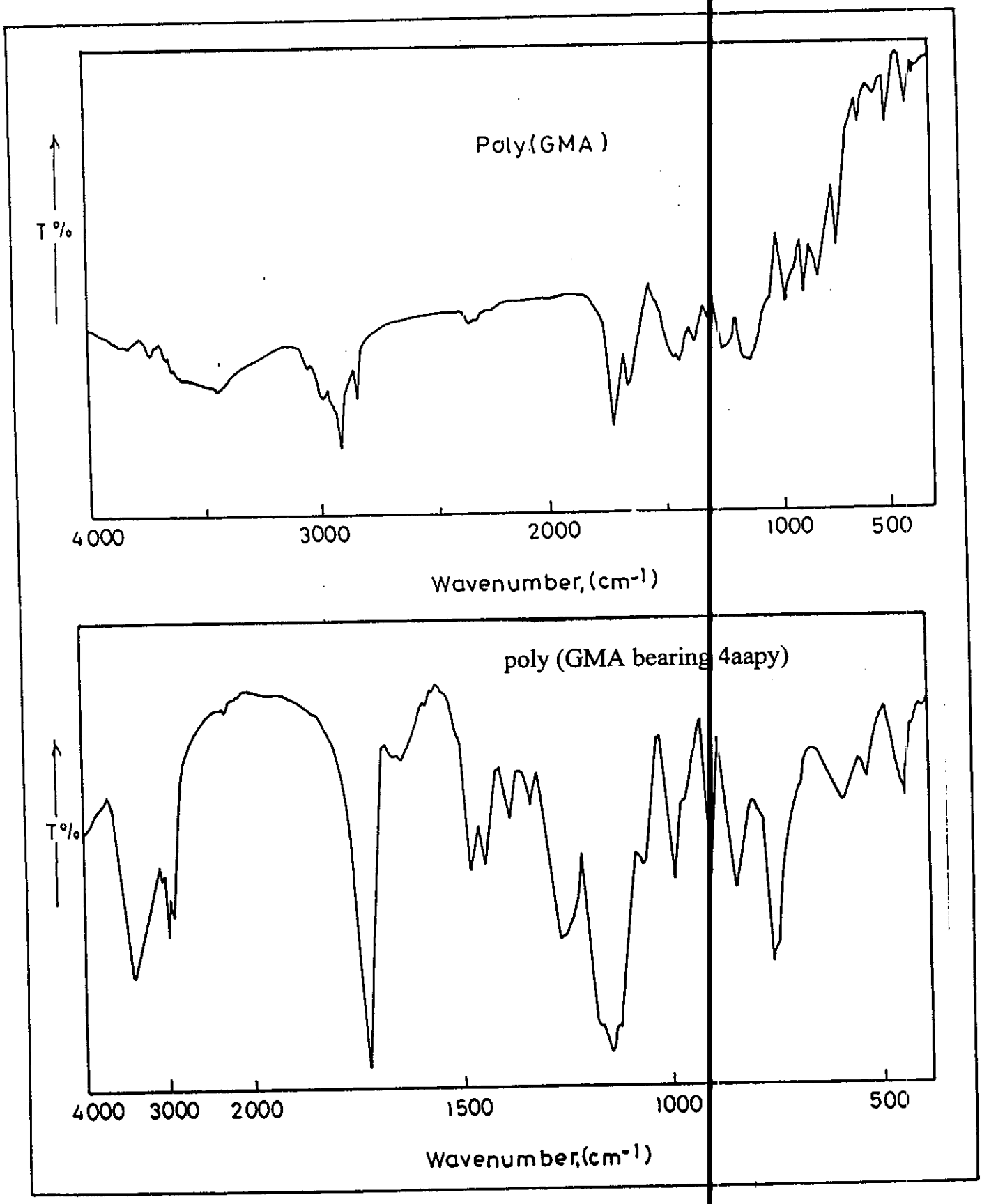


Fig. (4-a) : IR spectra of poly GMA (XIII) and poly (GMA bearing 4aapy) (XV)

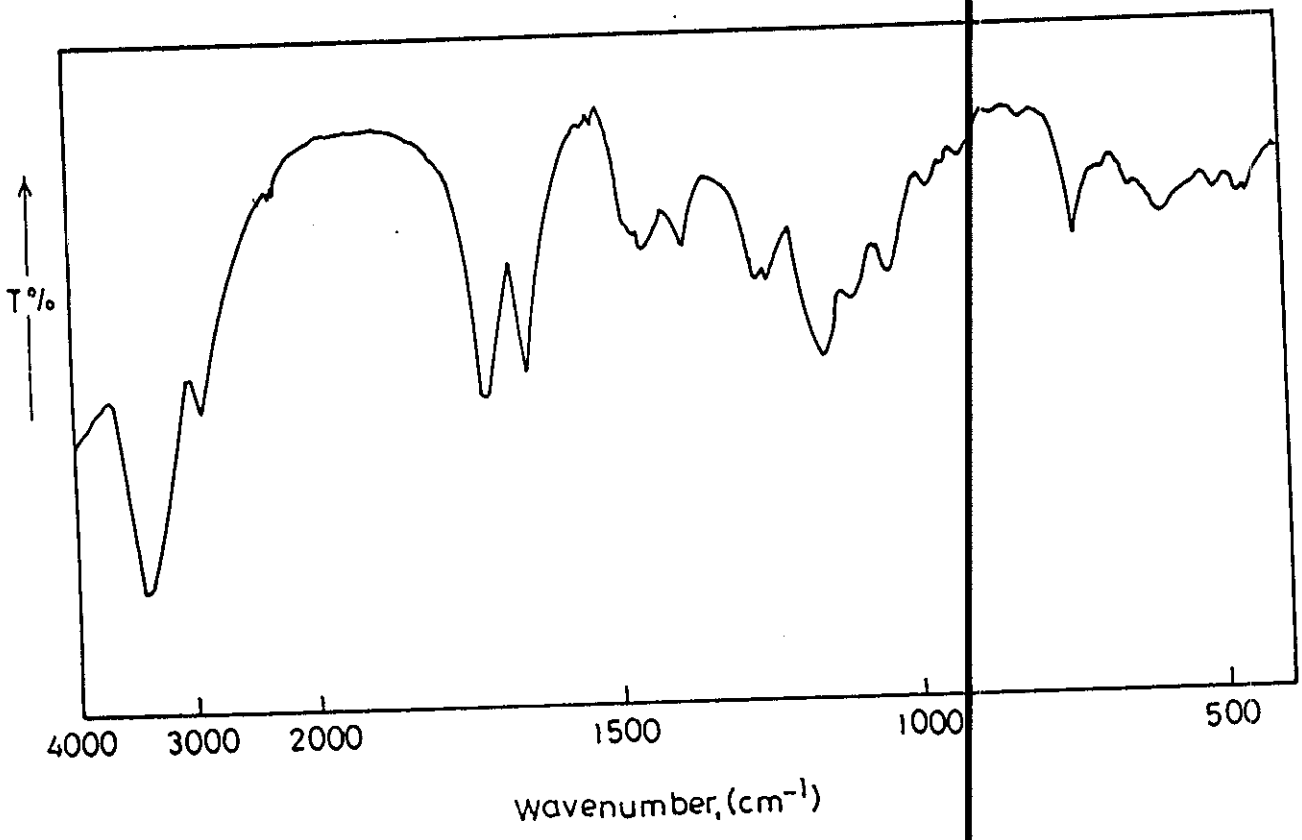


Fig. (4-b) : IR spectra of poly (GMA bearing 4aapy) copper complex (XVIII)

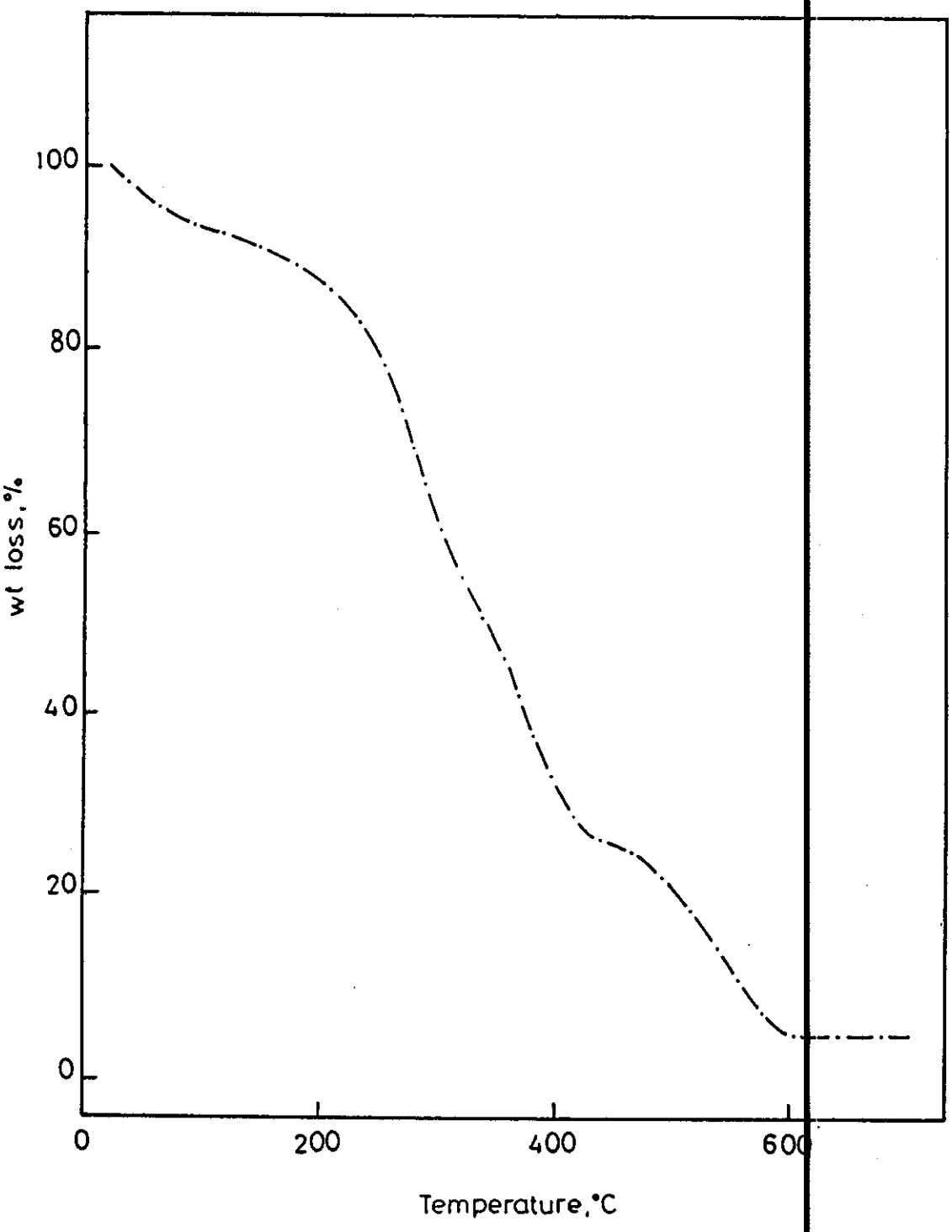


Fig. (5): TGA curve of poly (GMA bearing 4aapy) copper complex (XVIII).

3) Metal complexes of poly (GMA bearing 2ath) (XIX)

Again the bearing of GMA-polymer (XIII) by 2-Aminothiazole (as chelating ligand) was also takes place through the opening of the epoxy ring as reported for ethylenediamine and 4-Aminoantipyrine. Comparing the IR spectra of GMA-polymer (parent compound) and 2-Aminothiazole bearing chelating polymer (XV) obtained we can see that.

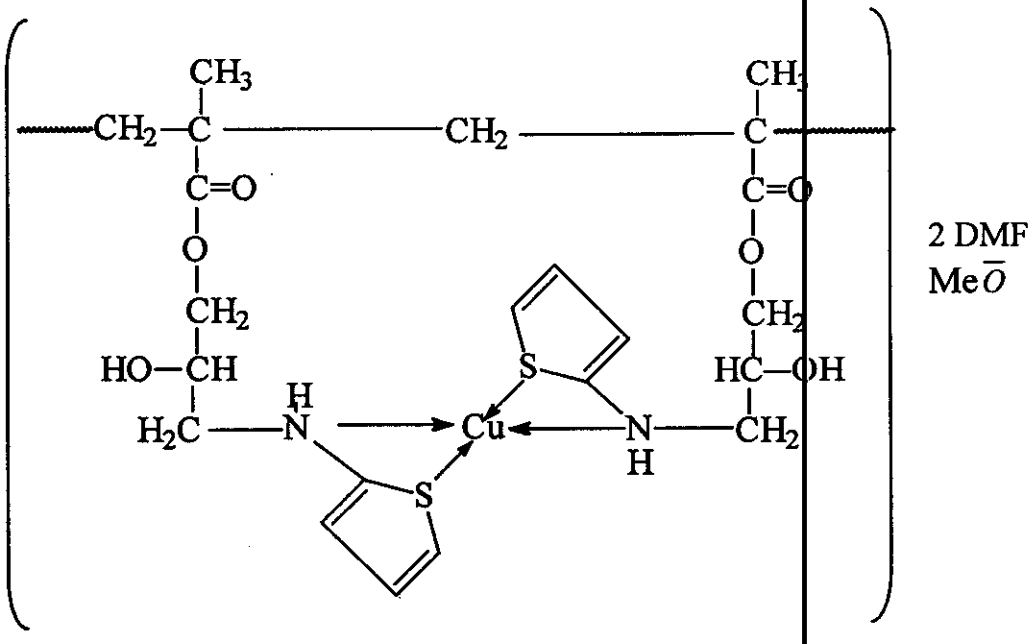
The spectrum of the chelating polymer is characterized by new peaks at 3420, 1630, 1380, 1070 and 750(split) cm^{-1} Fig. (6a-b). These peaks are assigned to νNH/OH, ν(C=C), νC-OH, νC-N and νC-S-C respectively[75,94].

The appearance of those bands confirm the bearing of GMA-polymer by 2-aminothiazole as a chelating molecule.

On the reaction with copper (II) chloride, the spectrum of the complex obtained show significant changes in the profile of the peaks from that of the ligand Fig. (6a-b). Some peaks such as νNH (3300 cm^{-1}), νC-N (1040 cm^{-1}) and ν(C-S-C) at 740 cm^{-} shifted to lower frequency. This behaviour indicate that the coordination mode taken place via N/S of NH group and sulpher atom of the thizole ring. The characteristic peaks of νOH (3420 cm^{-1}), νC-OH (1380 cm^{-1}) and νC=O (1730 cm^{-1}) show no shift from that of the chelating ligand. This indicate that these groups don't participate in the coordination mode. The spectrum of the complex show a new peak at 1650 cm^{-1}. This peak is assigned to νC=O of the dimethylformamide (DMF) which appears in the structure as a solvent of crystallization.

The TG study gives a weight loss (20.6%) at 267 °C corresponding two molecules of DMF Fig. (7). The magnetic moment measurement displays a diamagnetic properties (0.0 BM value) for the complex. This

indicate that the copper is copper (I). So the thiazole bearing polymer stabilize the oxidation state (I) for copper. The observed green colour for the solid complex may be attributed to the charge transfer (C.T.) transition[91]. The above data in addition to the elemental analysis table (1) suggest the following structure:



(XIX)

Table (1) : Elemental analysis and TG results of Poly (GMA bearing 4aapy)-Cu (XVIII) and Poly (GMA bearing 2ath)-Cu (XIX) complexes.

	C% cal. (F)	H% cal(F)	$\mu_{eff.}$ B.M.	Temp. TG °C	Weight loss % cal. (F)	Reaction
Poly(GMA bearing 4aapy)-Cu complex	44.9 (45.3)	5.9 (6.2)	1.31	210	12.3 (12.4)	Loss of 1.0 molecule (DMF)
Poly (GMA bearing 2ath)-Cu complex	44.7 (43.7)	6.2 (6.6)	0.0	267	20.6 (20.1)	Loss of 2.0 molecule (DMF)

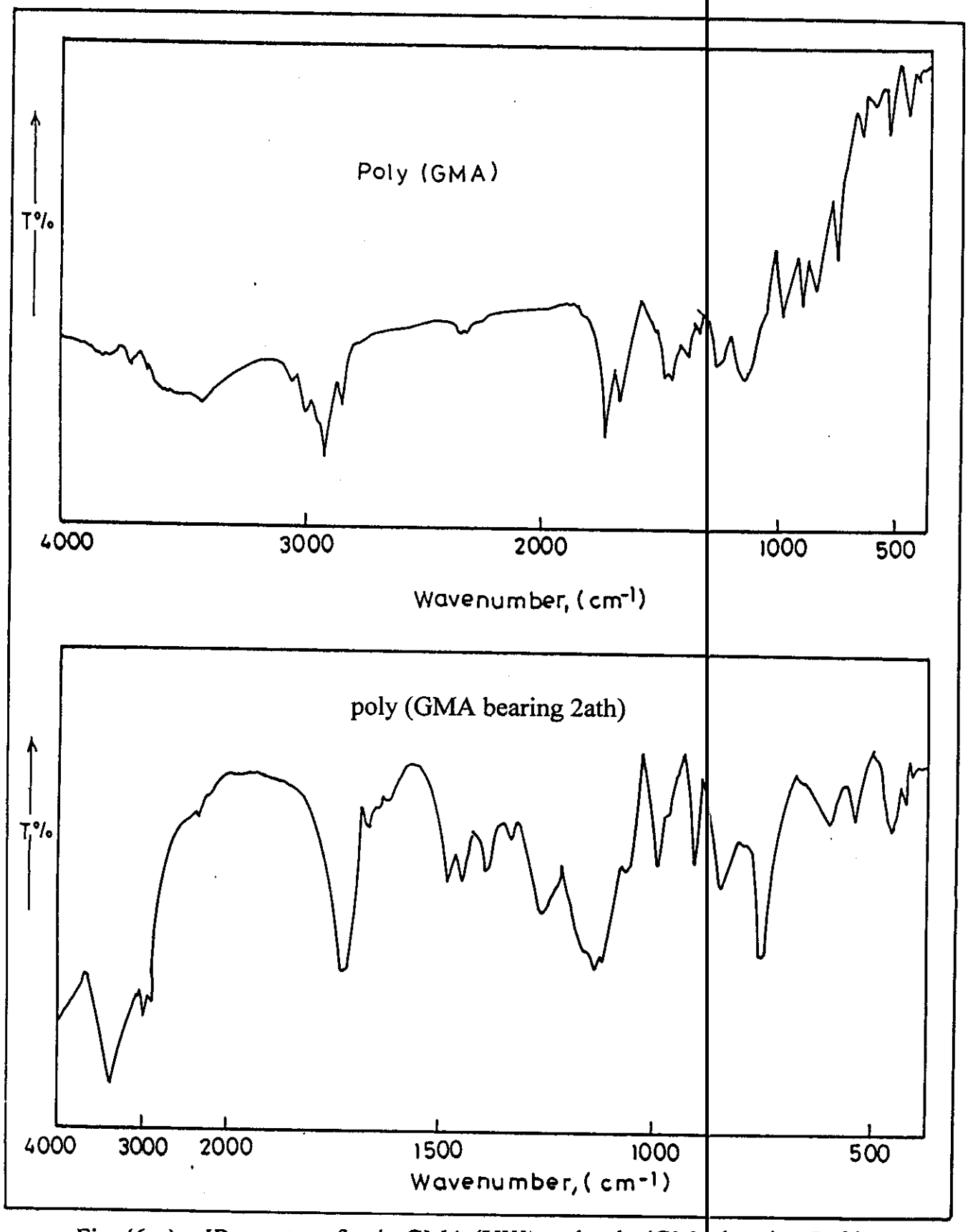


Fig. (6-a) : IR spectra of poly GMA (XIII) and poly (GMA bearing 2ath) (XVI).

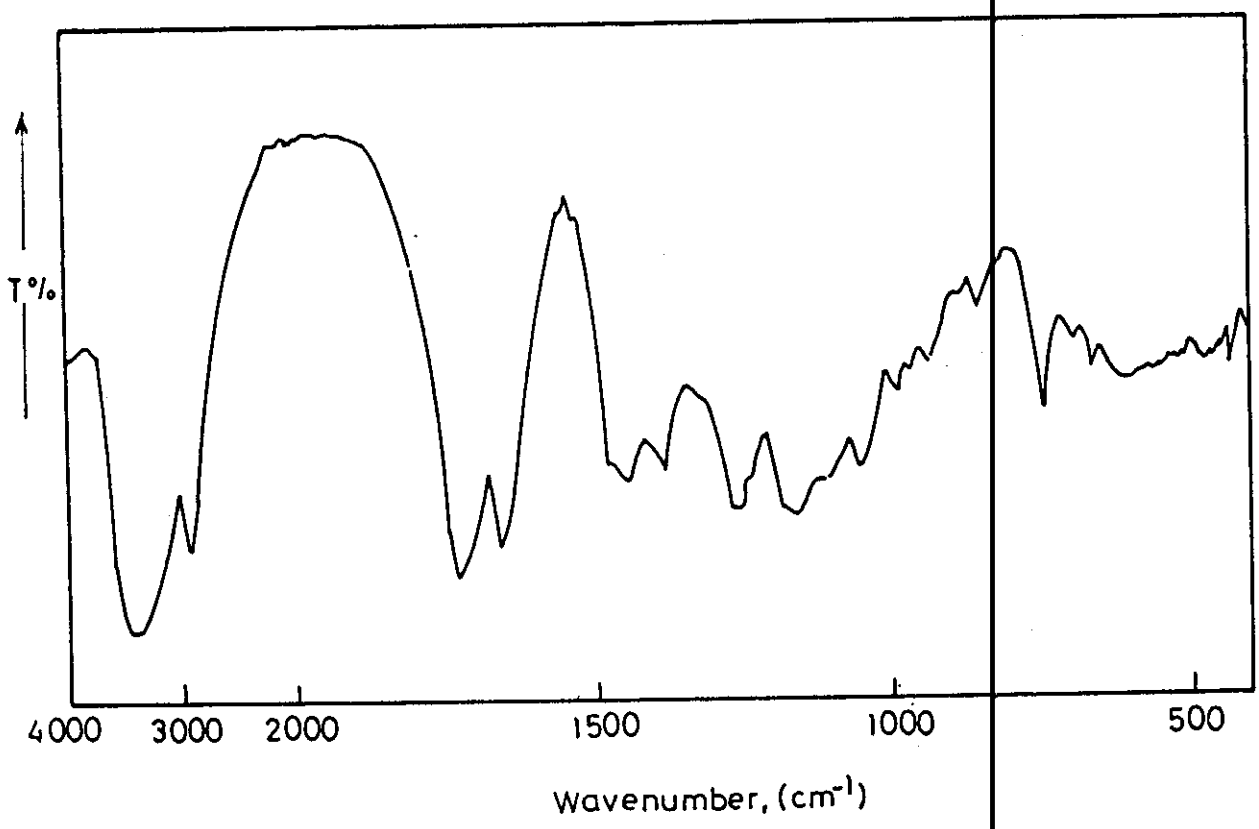


Fig. (6-b) : IR spectra of poly GMA (XIII) and poly (GMA bearing 2ath) copper complex (XIX).

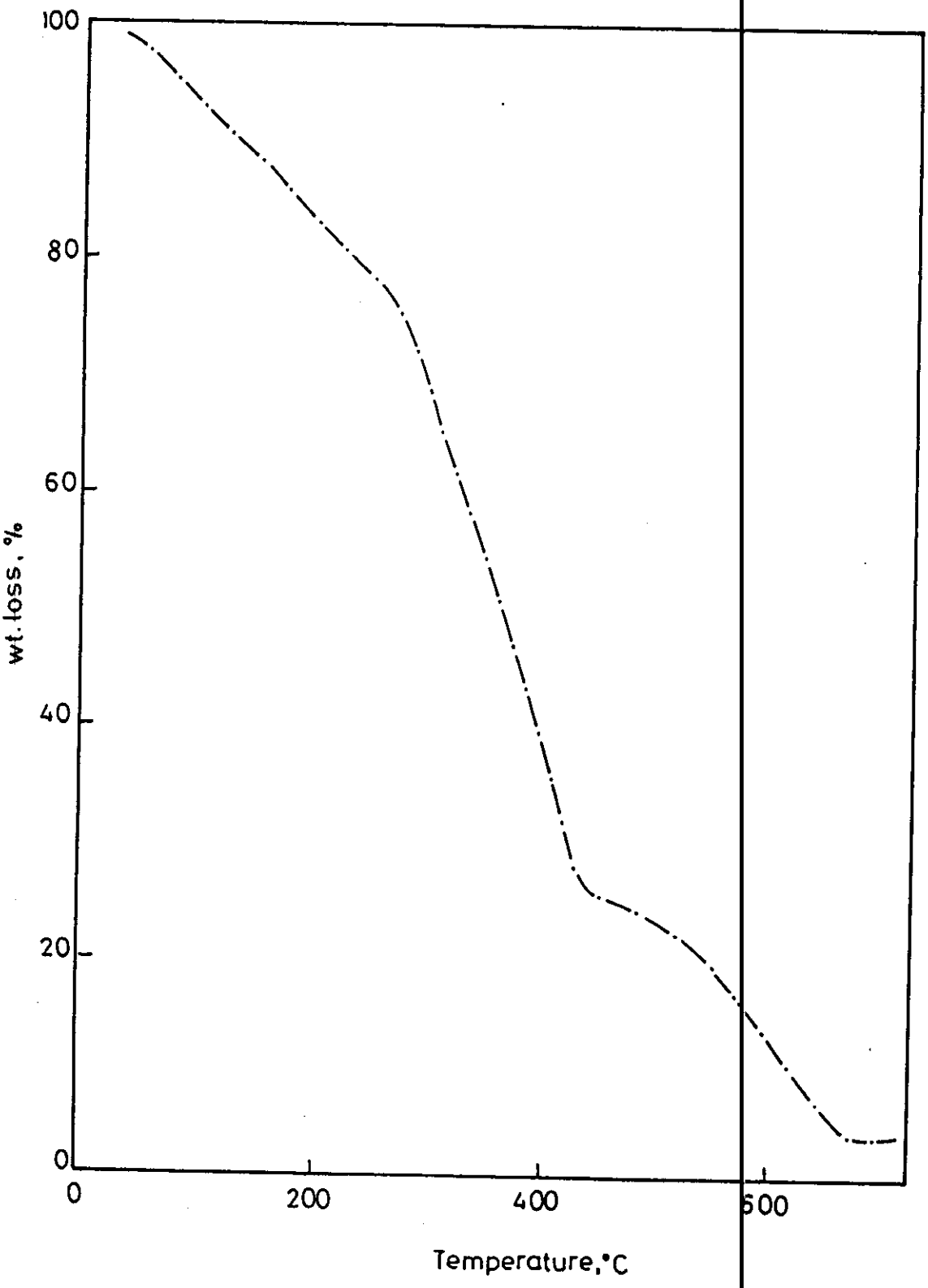


Fig. (7) : TGA curve of poly GMA (XIII) and poly (GMA bearing 2ath) (XVI).