E X P E R I M E N T A L

PYROLYSIS OF POLYCHELATES

II EXPERIMENTAL

II.1 General:

(i) Reagents and solvents:

All reagents and solvents used were of C.P. grade.

(ii) Analysis of products:

Analyses of new products were carried out for metal, nitrogen, carbon and hydrogen as required by known micro methods.

(iii) Melting points:

All melting points recorded herein are uncorrected.

(iv) IR spectra:

IR absorption spectra of the compounds in KBr pellet form were obtained on Infracord model of Perkin-Elmer or Beckman IR-5 spectrophotometer.

(v) Electrical resistivity:

Electrical resistivity of the compounds in the form of pressed pellet was measured on Ellico's Million megohmmeter Model RM-70 at room temperature.

(vi) Magnetic susceptibility:

Magnetic susceptibility of the metal chelates was determined on Gouy's magnetic balance at room temperature.

(vii) Thermal analysis:

Thermal analyses (DTA and TGA) of the compounds were obtained under the conditions of static air using Fisher thermal analysis equipment with Cahn electrobalance.

The observations and results of the various determinations for different compounds are given at appropriate places in the following pages.

II.2 Polychelates of Chloranilic acid and their Pyrolysis:

(i) Cobalt(II), Nickel(II), Copper(II) Lead(II), Iron(II) and Uranyl(II) chelates of chloranilic acid:

Metal salt (0.01 mole) dissolved in alcohol with few drops of aqueous acetic acid, was added slowly to the solution of chloranilic acid (0.01 mole) in alcohol with continuous stirring. The mixture was kept over-night and filtered. The precipitates were washed with hot water and alcohol and dried. These polychelates were found insoluble in common organic solvents. They were analysed and their magnetic susceptibility and electrical resistivity were determined and their IR spectra and thermograms (DTA and TGA) were obtained. The results are presented in tables II.2(a) to (c) and figures II.2(i) to(x).

(ii) Pyrolysis of Polychelates:

These compounds, were pyrolyzed in quartz tube with continuous evacuation at 310-30°C and 530-60°C. Residual product left in the tube was taken out, washed with alcohol and acetone and dried. The products were analysed and their magnetic susceptibility and IR spectra were obtained. The results are presented in tables II.2(d) to (g) and figures II.2(i) to (vi).

II.3 Polychelates of 3,3'-diacetyl 4,4'-dihydroxy diphenyl sulphone and their pyrolysis:

(i) 3:3'-diacetyl 4:4'-dihydroxy diphenyl sulphone (DAS):

(a) Diacetate derivative of 4:4'-dihydroxy diphenyl sulphone : To 10 gms of 4:4'-dihydroxy diphenyl sulphone were added 23 ml of acetic anhydride and few drops of pyridine. This mixture was warmed to 60° - 70°C for about 15 minutes when clear solution was obtained. The solution was poured over crushed ice. The white precipitates were

TABLE II. 2(a)

Polychelates of Chloranilic acid (CA)

melting point > 360°C

No	Metal in Polychelates	Polychelate	Colour	Formula	Analysis (found)		Analysis (required)	
					% C	% H	% C	% H
1	Cobalt(II)	CoCA	redish brown	$CoC_6H_8Cl_2O_8$	20.9	2.9	21.4	2.4
2	Nickel(II)	NiCA	dark green	$NiC_6H_8Cl_2O_8$	20.8	3.0	21.4	2.4
3	Copper(II)	CuCA	green	$CuC_6H_2Cl_2O_5$	24.3	0.5	24.9	0.7
4	manganese(II)	MnCA	brownish black	$MnC_6H_5Cl_2O_{6.5}$	23.4	1.8	23.4	1.6
5	Iron(II)	FeCA	dark green	$FeC_6H_7Cl_2O_{7.5}$	21.6	1.8	22.1	2.1
6	Lead(II)	PbCA	brown	$PbC_6H_2Cl_2O_5$	16.9	0.9	16.8	0.5
7	Uranyl(II)	UCA	brown	$UC_6H_1Cl_2O_{6.5}$	15.4	0.5	14.8	0.2

TABLE II. 2(b)

Magnetic susceptibility of Polychelates of CA

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
1	CoCA	32	28.0	- 134
2	NiCA	32	12.1	- 136
3	CuCA	32	5.2	- 100
4	MnCA	33	47.0	- 115
5	FeCA	33	39.2	- 126
6	PbCA	33	Diam.	-
7	UCA	33	Diam.	-

TABLE II. 2(c)

Solid State Electrical Resistance of Polychelates of CA

No	Polychelate	Resistance of pellet R(ohm)x10^{-9}	thickness/area of pellet l/a (cm^{-1})	Temperature (°C)
1	CoCA	1.5	0.1443	32
2	NiCA	1.2	0.2130	32
3	CuCA	96	0.2082	32
4	MnCA	1.05	0.1530	32
5	FeCA	1.65	0.2634	32
6	PbCA	0.975	0.2750	32
7	UCA	195	0.2498	32

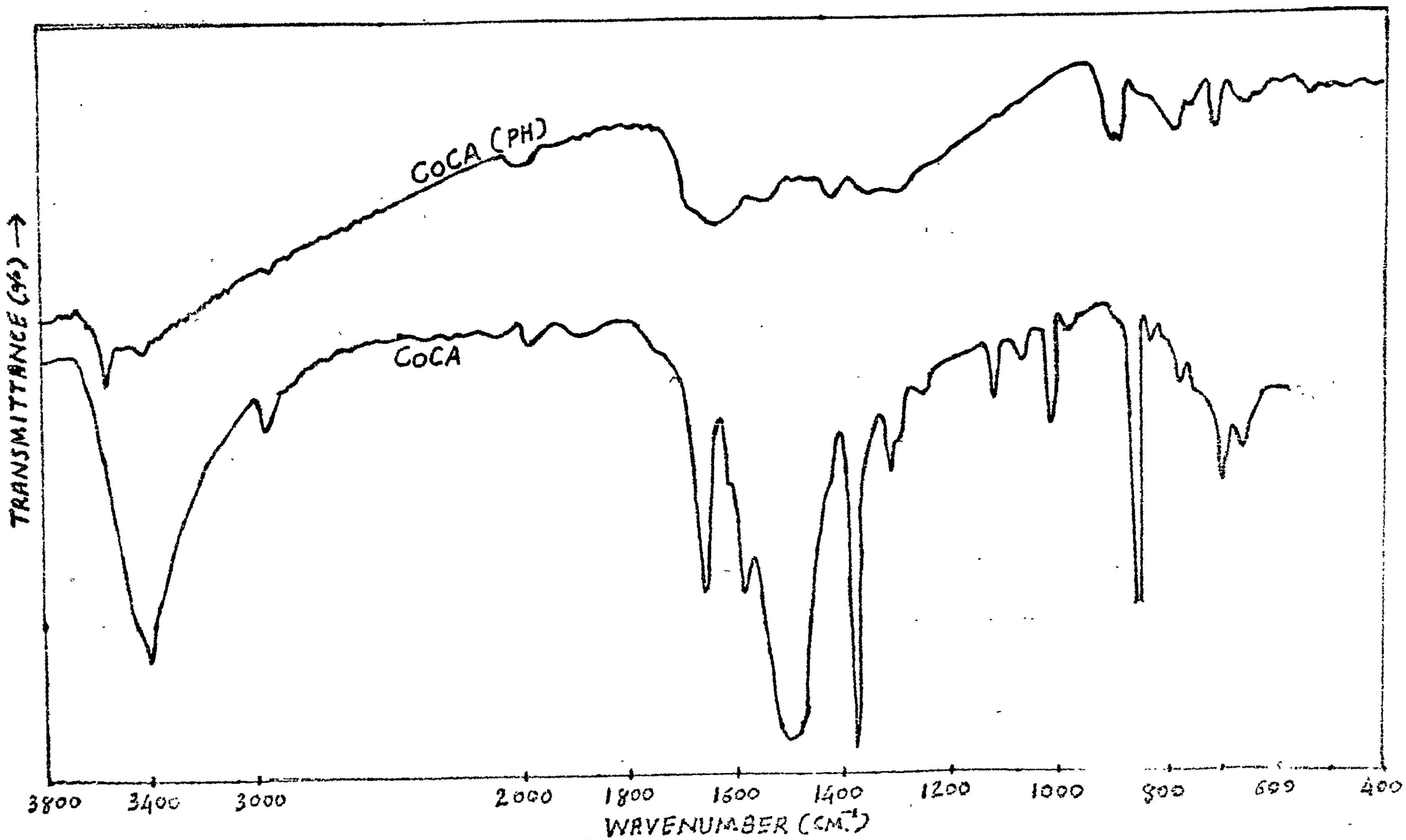

Fig. II. 2.(i) IR spectra of CoCA and CoCA (PH)

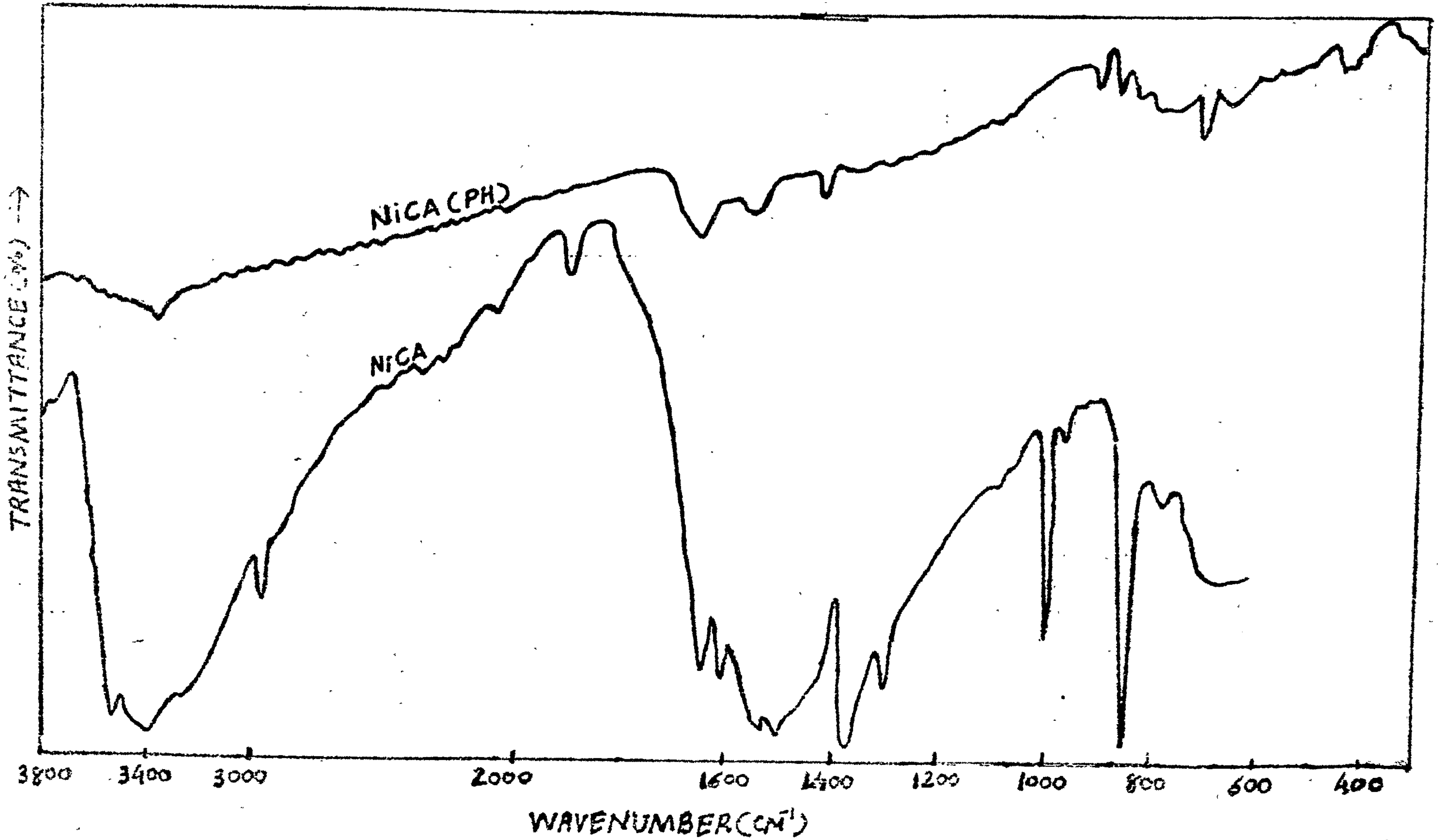

Fig. II. 2.(ii) IR spectra of NiCA and NiCA (PH)

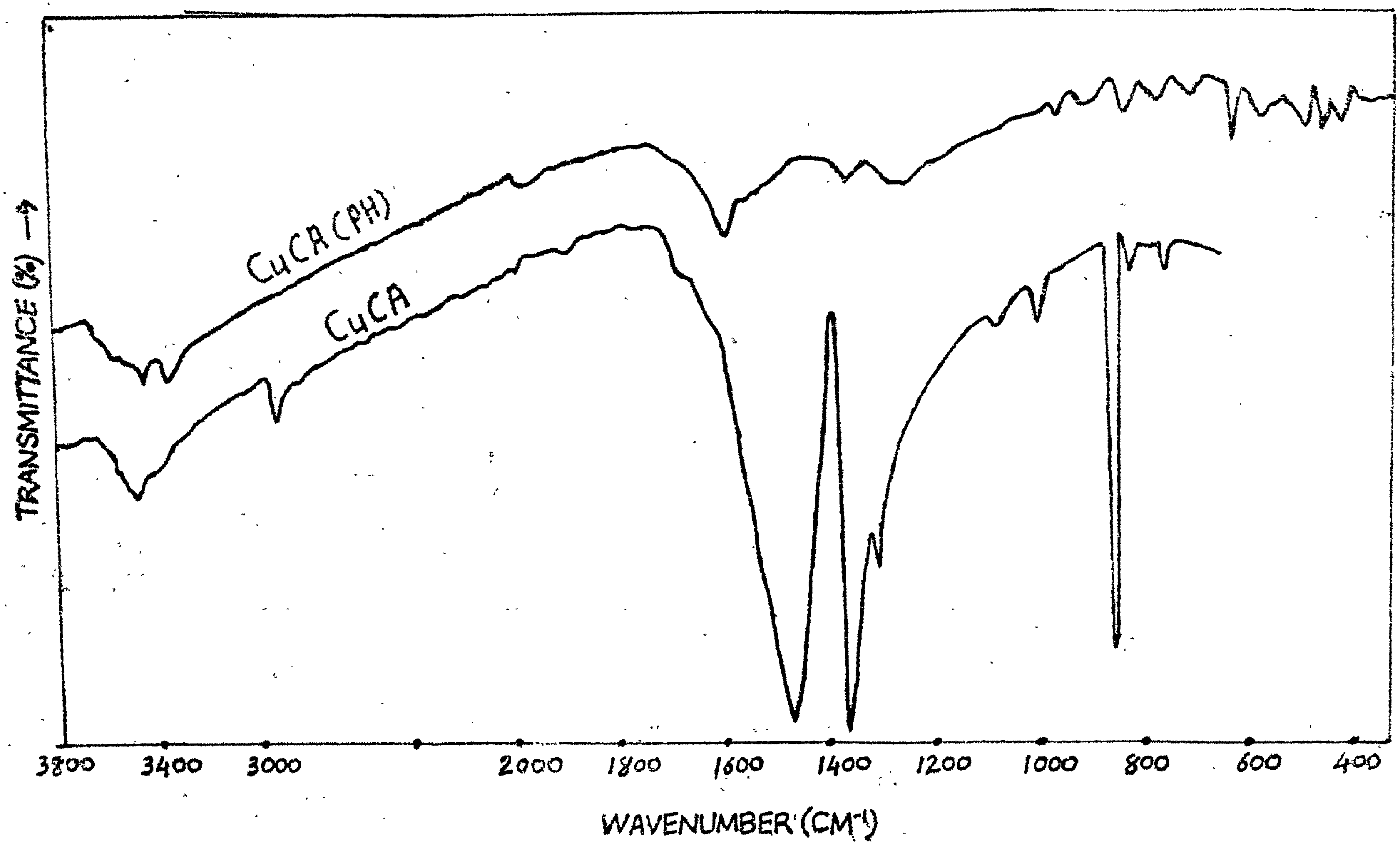

Fig. II.2(iii) IR spectra of CuCA and CuCA(PH)

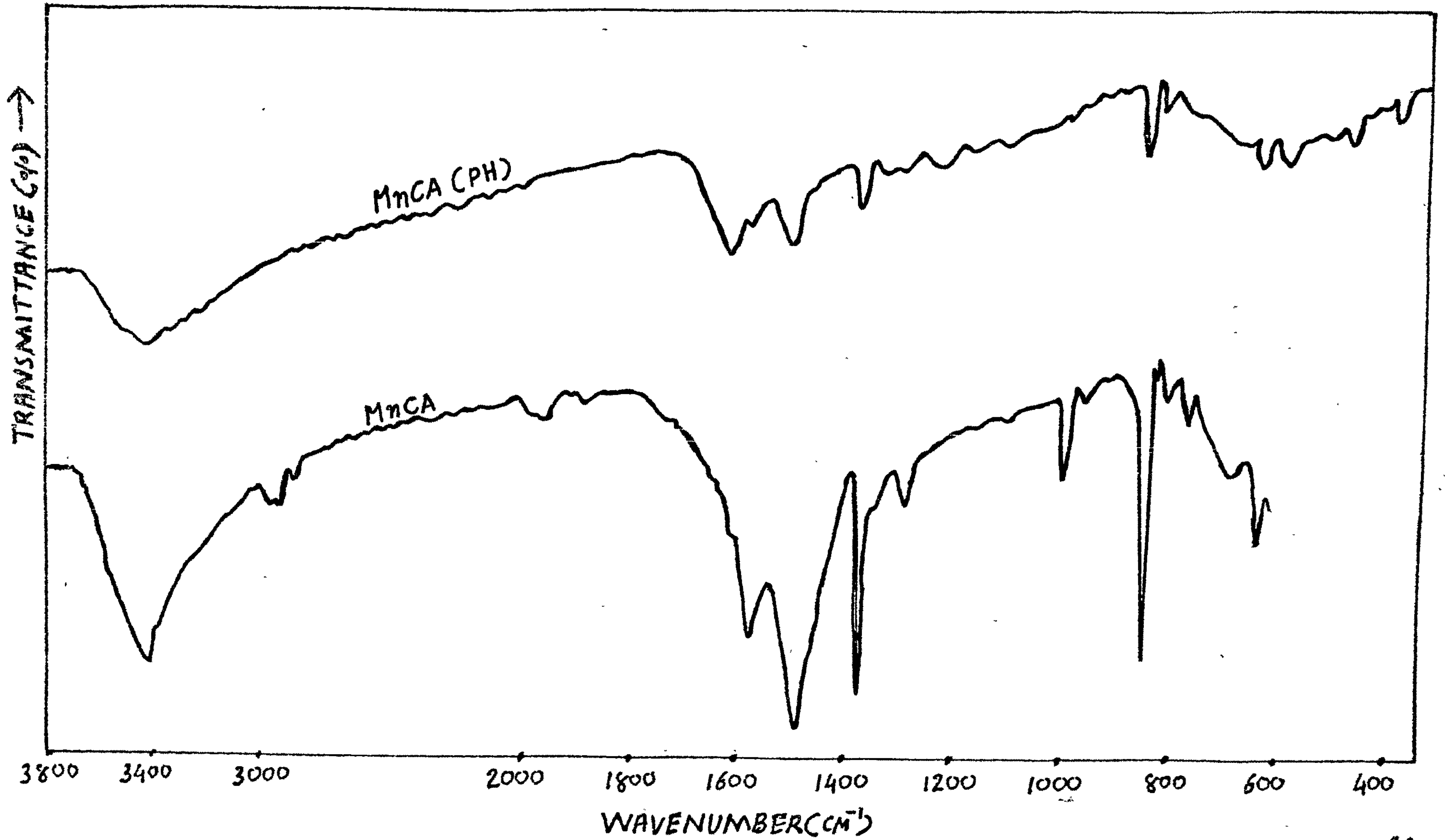

Fig. II.2 (iv). IR spectra of MnCA and MnCA (PH)

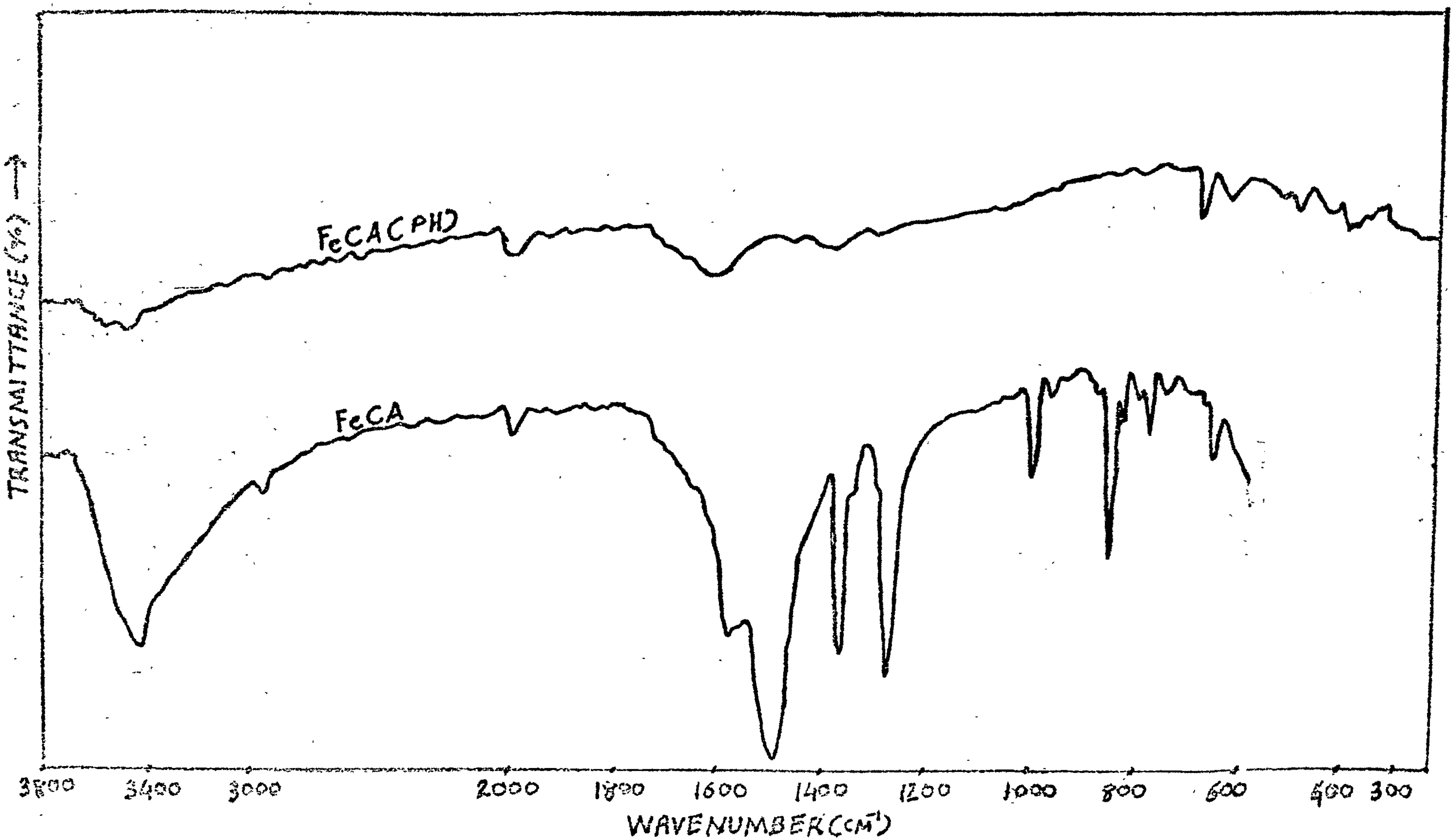

Fig. II. 2 (V). IR spectra of FeCA and FeCA (PH)

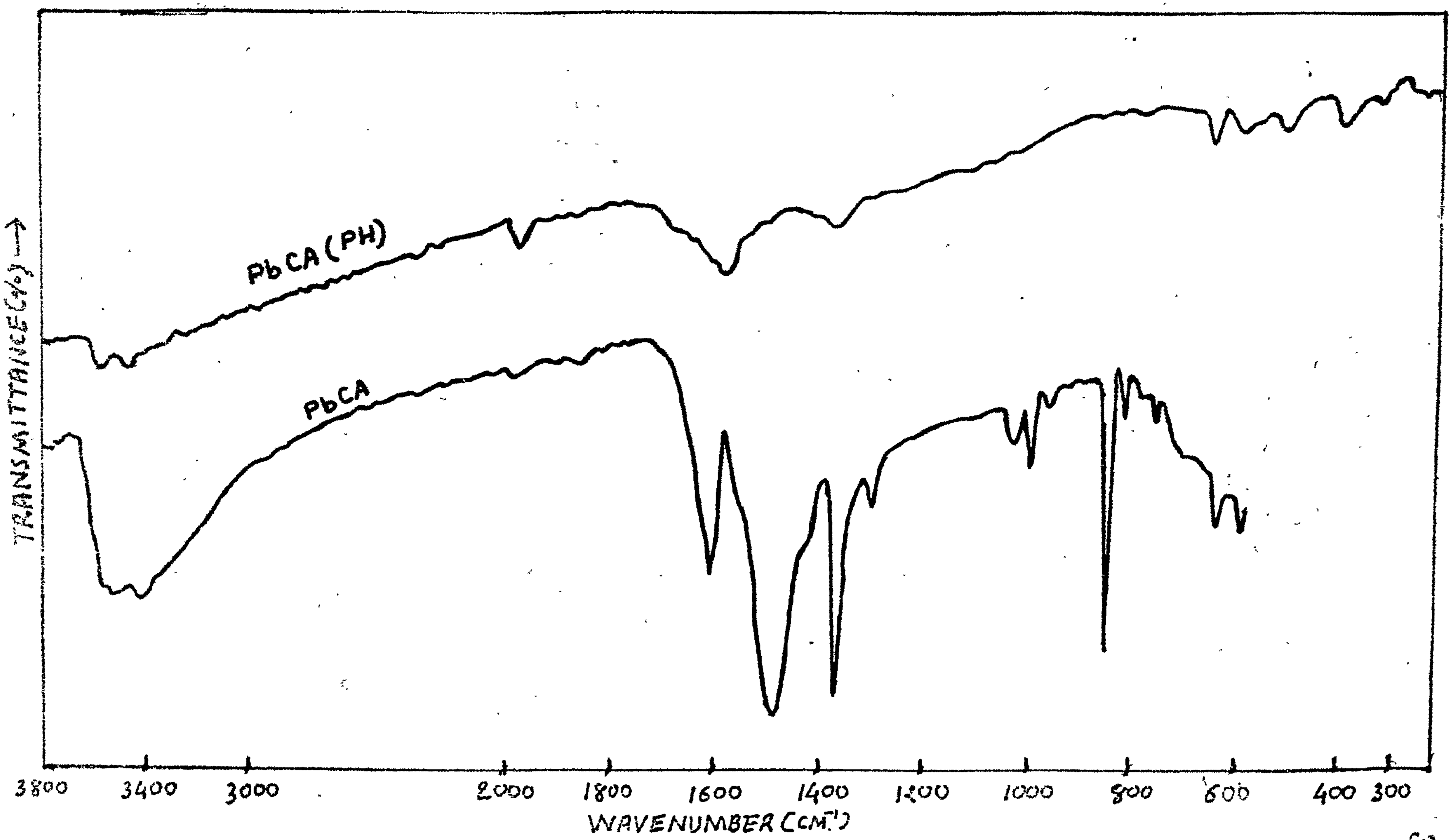

Fig. II. 2. (vi) IR spectra of PbCA and PbCA (PH)

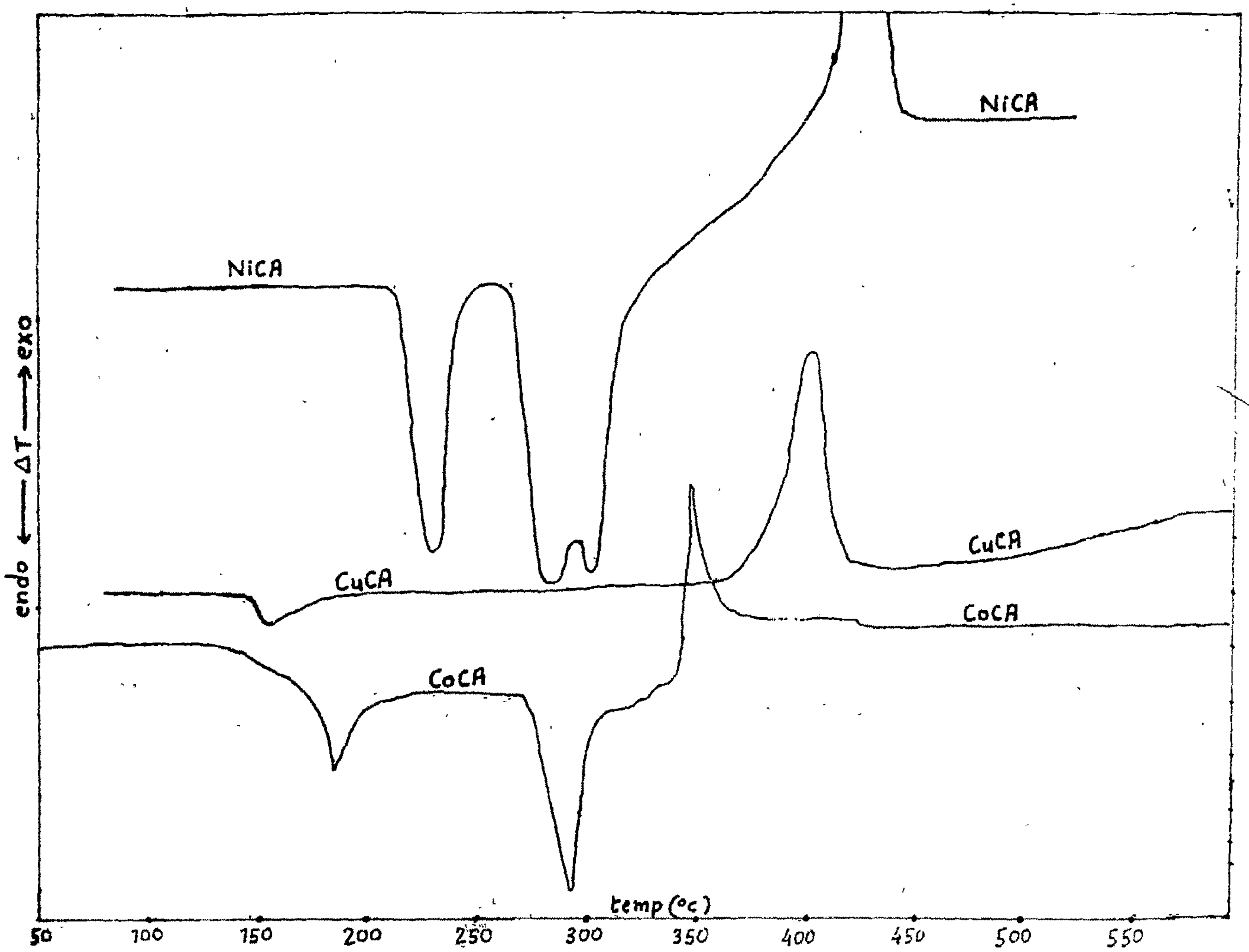

Fig. II. 2.(vii). DTA curves of CoCA, NiCA and CuCA.

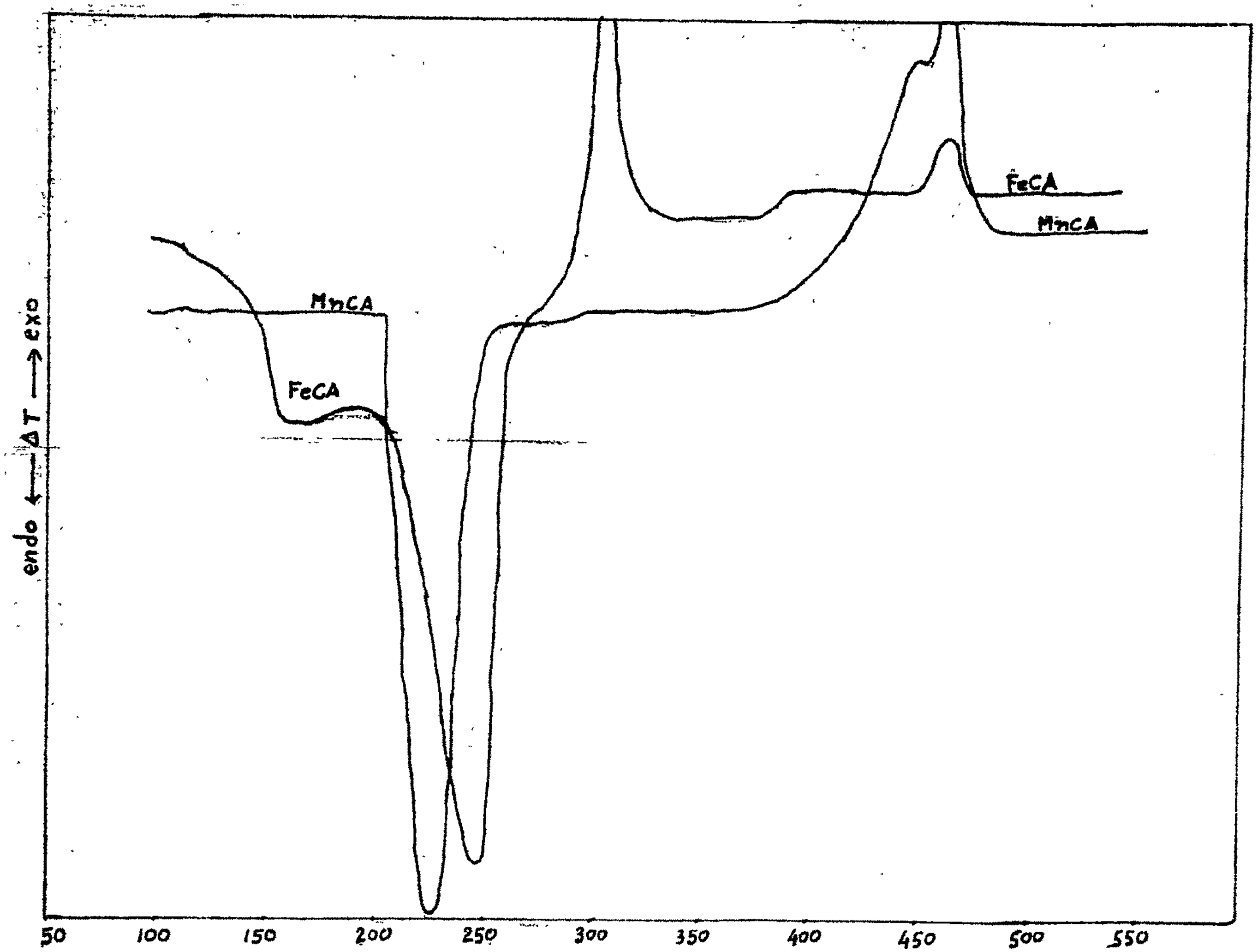

Fig. II 2 (viii). DTA curves of MnCA and FeCA.

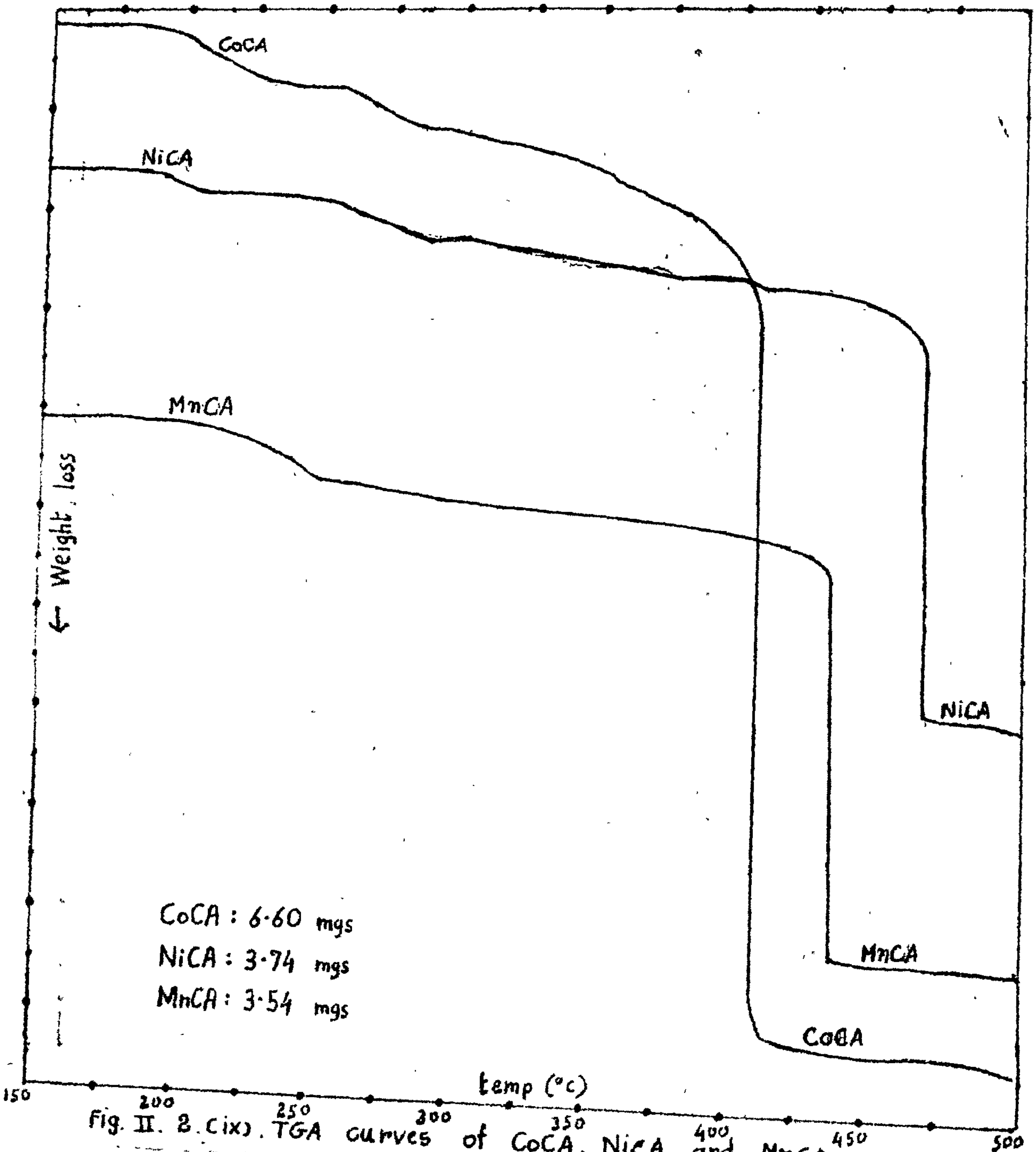

Fig. II. 2.(ix). TGA curves of CoCA, NiCA and MnCA

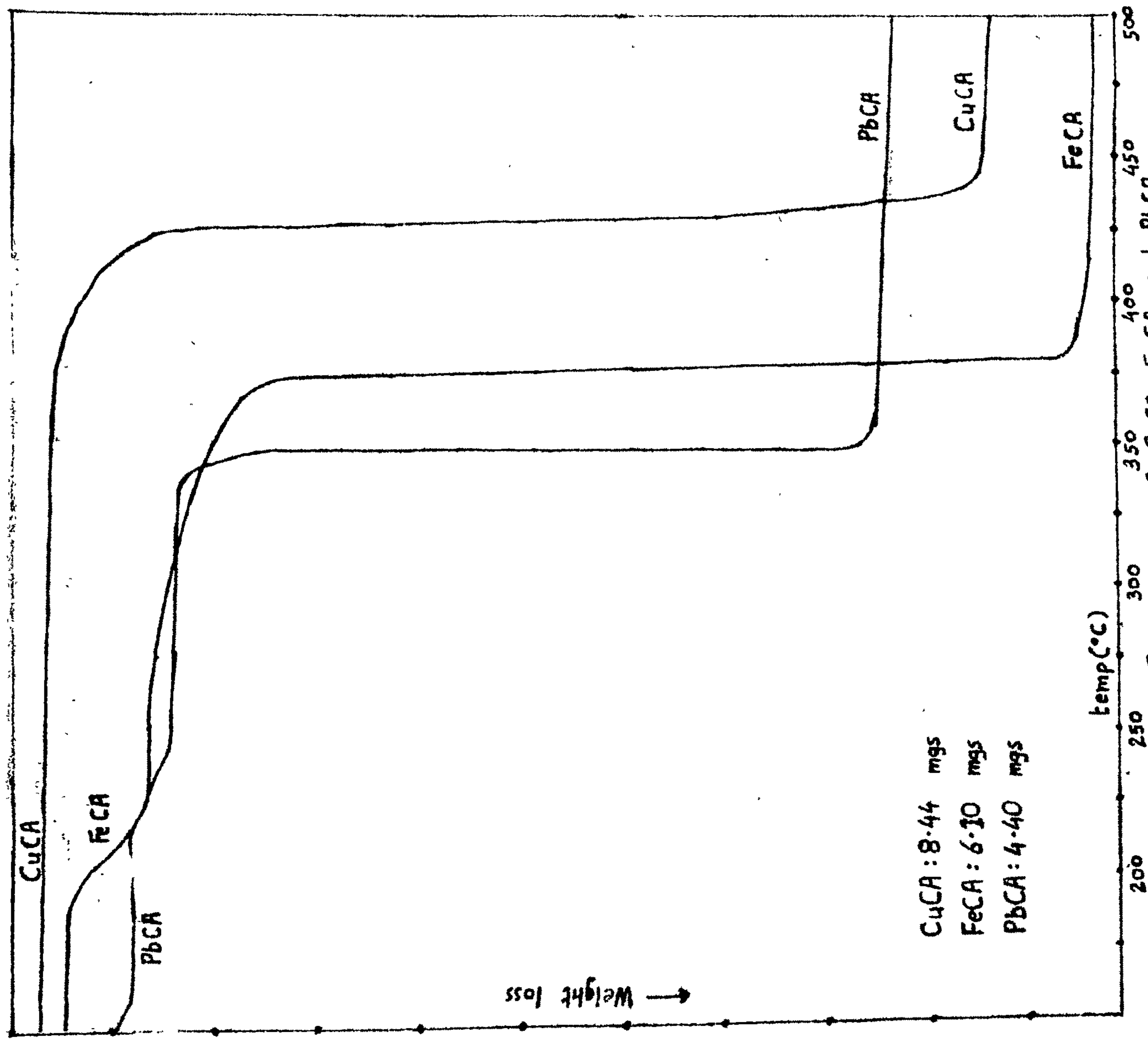

Fig. II.2(X). TGA curves of CuCA, FeCA, and PbCA

TABLE II.2 (d)

Pyrolyzed Polychelates of CA (pyrolyzed at 310-30°C)

No	Metal in Polychelate	Polychelate	Colour	Formula	Analysis		
					% C found/required	%H found/required	%M found/required
1	Cobalt(II)	CoCA(PL)	black	$CoC_6H_{14}O_{11}Cl_2$	17.9/18.4	3.5/3.6	15.2/15.0
2	Nickel(II)	NiCA(PL)	black	$NiC_6H_{10}O_9Cl_2$	19.4/20.2	3.0/2.8	16.1/16.5
3	Copper(II)	CuCA(PL)	black	$CuC_6H_2O_5Cl_2$	24.3/25.0	1.1/0.7	22.3/22.0
4	Manganese(II)	MnCA(PL)	black	$MnC_6O_4Cl_2$	27.1/27.5	-	21.4/21.0
5	Iron(II)	FeCA(PL)	black	$FeC_6H_4O_6Cl_2$	24.8/24.1	1.6/1.3	18.3/18.7
6	Lead(II)	PbCA(PL)	black	$PbC_6O_4Cl_2$	17.0/17.4	-	50.6/50.0

TABLE II.2(e)

Magnetic Susceptibility of Pyrolyzed Polychelates of CA

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
1	CoCA(PL)	32	25.0	- 163
2	NiCA(PL)	32	12.0	- 142
3	CuCA(PL)	32	6.0	- 100
4	MnCA(PL)	32	49.3	- 89
5	FeCA(PL)	32	50.0	- 110
6	PbCA(PL)	32	3.9	- 101

TABLE II.2(f)

Pyrolyzed Polychelates of CA
(pyrolyzed at 530-60°C)

No	Metal in polychelate	Polychelate	Colour	Formula	Analysis (found)/(required) % C	% H	% M
1	Cobalt(II)	CoCA(PH)	black	$CoC_6H_3O_{5.5}$	32.0 / 32.4	0.9 / 1.4	26.2 / 26.6
2	Nickel(II)	NiCA(PH)	black	$Ni_3C_6H_{14}O_{13}$	15.1 / 15.2	4.0 / 2.9	38.6 / 37.3
3	Copper(II)	CuCA(PH)	black	$Cu_3C_6H_6O_9$	17.2 / 17.4	2.0 / 1.4	46.0 / 46.0
4	Manganese(II)	MnCA(PH)	black	$MnC_6H_{11}O_{4.5}$	37.5 / 36.0	0.8 / 0.5	27.5 / 27.5
5	Iron(II)	*FeCA(PH)	black	$Fe_3C_6H_2O_7$	20.9 / 20.4	0.4 / 0.6	46.4 / 47.4
6	Lead(II)	*PbCA(PH)	black	$PbC_6H_{16}O_{12}$	13.9 / 14.9	3.4 / 3.3	43.0 / 42.2

TABLE II.2(g)

Magnetic Susceptibility of Pyrolyzed Polychelates of CA

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
1	CoCA(PH)	32	45.2	- 71
2	NiCA(PH)	32	28.0	- 56
3	CuCA(PH)	33	8.9	- 42
4	MnCA(PH)	32	74.0	- 61
5	*FeCA(PH)	32	150.0	- 33
6	*PbCA(PH)	32	5.5	- 151

filtered, washed with water and dried.

(b) DAS (Fries migration method): 10 gms of the above diester derivative and 33 gms of anhydrous aluminium chloride were transferred to 250 ml round bottom flask and heated in oil bath at 140°C for one hour with air condenser having guard tube at the top. The temperature was raised to 150°C for five hours and then the mass was cooled. The solid mass was powdered and was discharged in ice cooled water with hydrochloric acid with continuous stirring. The gummy precipitates were filtered, washed with 25% HCl and finally with water. The product was recrystallized from alcohol or acetic acid. The melting point was found to be 193-94° C. It was tested for its ketonic group with the reagent 2:4-dinitro phenyl hydrazine when the hydrazone derivative was obtained with melting point 268-69°C.

Analysis	found	% C 58.1,	% H 4.1
$C_{16}H_{14}O_6S$	requires	% C 57.5,	% H 4.2

(ii) Copper(II), Cobalt(II) and Nickel(II) polychelates of DAS

Metal acetate (0.01 mole) and ligand (0.01 mole) dissolved in ammonia separately were mixed with continuous stirring and left over-night. The precipitates were filtered, washed with alcohol and dried. These polychelates were found insoluble in common organic solvents. Their analysis, magnetic susceptibility and electrical conductivity were determined and their IR spectra and thermograms (DTA and TGA) were obtained. The results are given in tables II.3 (a) to (c) and figures II.3 (i) to (iii).

(iii) Pyrolysis of Polyechelates:

These compounds were pyrolyzed in quartz tube under continuous evacuation for one hour at 310-30°C. The residual products were collected, washed with alcohol and acetone and dried. Their analysis, magnetic susceptibility and IR spectra were obtained. The results are given in tables II.3(d) and (e) and figure II.3(i)

II.4. Polychelates of 2,4-dinitroso resorcinol and their Pyrolysis:

(i) 2:4-dinitroso-resorcinol (DNR): 22 gms of resorcinol, 9 gms of sodium hydroxide and 27.6 gms of $NaNO_2$ were dissolved in cold water to keep the temperature 0-5°C. 50% H_2SO_4 was slowly added to the solution with vigorous stirring till the pH of the solution became 4. The yellow precipitates were filtered, washed with cold water and little aqueous alcohol, dried at 60°C, and re-crystallized from

TABLE II. 3(a)

Polychelates of 3,3'-diacetyl 4,4'-dihydroxy diphenol Sulphone (DAS)
melting point : > 360°C

No.	Metal in Polychelate	Polychelate	Colour	Formula	Analysis (found)/(required) % C	% H	% N	% M
1	Cobalt(II)	CoDAS	reddish brown	$CoC_{16}H_{18}N_2O_6S$	$\frac{45.4}{45.2}$	$\frac{4.6}{4.2}$	$\frac{7.4}{6.6}$	$\frac{13.7}{13.8}$
2	Nickel(II)	NiDAS	yellow	$NiC_{16}H_{18}N_2O_6S$	$\frac{45.8}{45.2}$	$\frac{4.2}{4.2}$	$\frac{6.4}{6.6}$	$\frac{13.6}{13.8}$
3	Copper(II)	CuDAS	grey	$CuC_{16}H_{18}N_2O_6S$	$\frac{45.3}{44.7}$	$\frac{4.0}{4.2}$	$\frac{6.4}{6.5}$	$\frac{13.8}{14.8}$

TABLE II. 3(b)

Magnetic Susceptibility of Polychelates of DAS

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
1	CoDAS	33	25.0	- 217
2	NiDAS	33	13.2	- 217
3	CuDAS	33	4.1	- 217

TABLE II. 3(c)

Solid State Electrical Resistance of Polychelates of DAS

No	Polychelate	Resistance of pellet R(ohm) x 10^{-9}	Thickness/area of pellet l/a (cm^{-1})	Temperature (°C)
1	CoDAS	0.46	0.1414	33
2	NiDAS	7.5	0.2130	33
3	CuDAS	1.8	0.2382	33

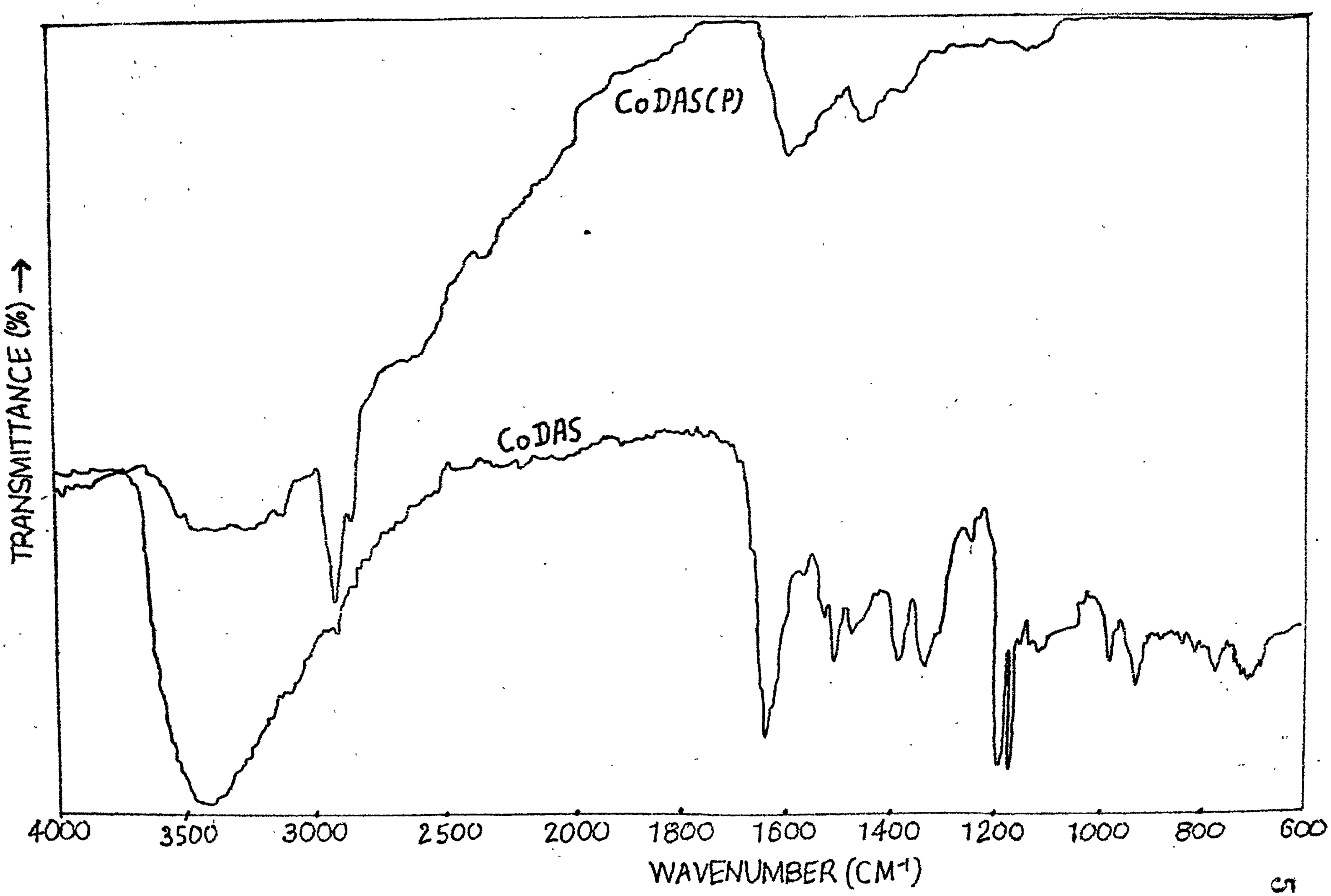

Fig.II.3(i) IR spectra of CoDAS and CoDAS(P)

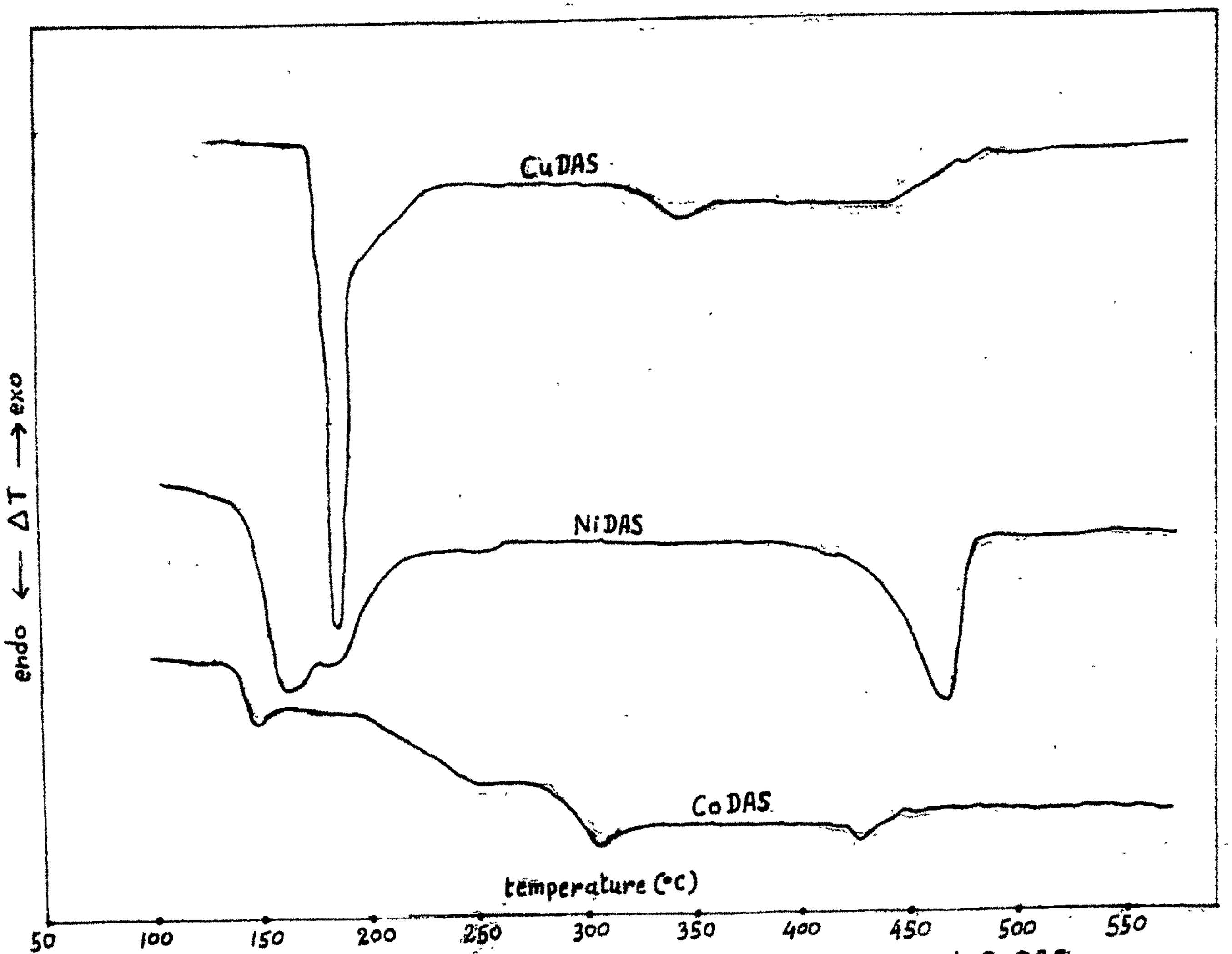

Fig. II.3 (ii). DTA curves of CoDAS, NiDAS and CuDAS

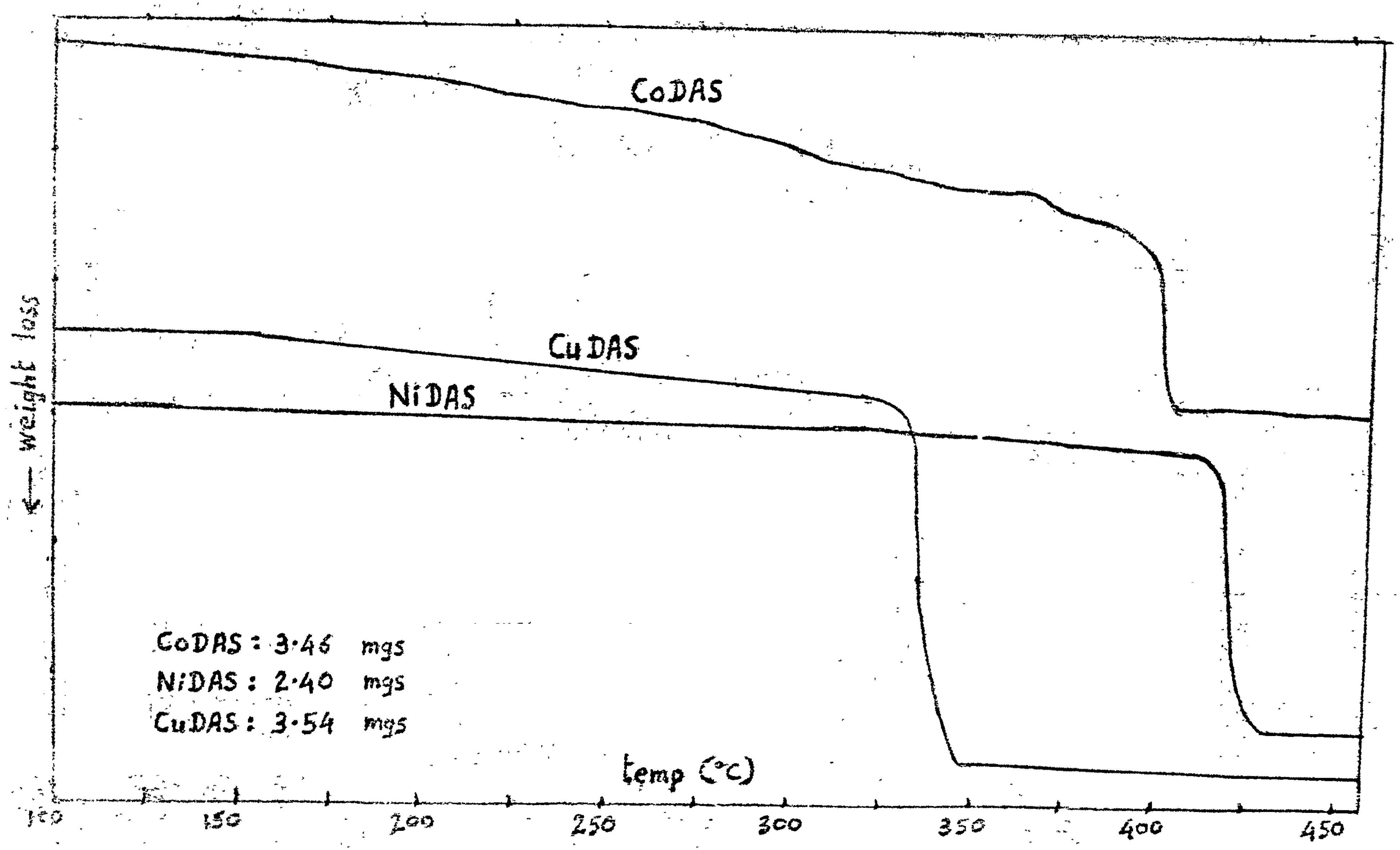

Fig. II.3 (iii). TGA curves of CoDAS, NiDAS and CuDAS

TABLE II.3(d)

Pyrolyzed Polychelates of DAS
(temperature of pyrolysis 410-430°C)
melting point: > 360°C

No	Metal in Polychelate	Polychelate	Colour	Formula	Analysis (found)/(required) % C	% H	% N	%M
1	Co	CoDAS(P)	black	$Co_2C_{32}H_{26}N_2O_{14}S_2$	44.8 / 45.5	3.1 / 3.1	2.8 / 3.3	14.4 / 14.0
2	Ni	NiDAS (P)	black	$Ni_2C_{32}H_{22}N_2O_{12}S_2$	49.3 / 47.6	2.9 / 2.7	3.2 / 3.5	15.6 / 14.5
3	Cu	CuDAS(P)	black	$Cu_2C_{32}H_{20}N_{0.66}O_{13}S_2$	47.7 / 47.3	3.3 / 2.5	1.0 / 1.1	16.0 / 15.6

TABLE II 3(e)

Magnetic Susceptibility of Pyrolyzed Polychelates of DAS

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
1	CoDAS(P)	33	24.3	- 183
2	NiDAS(P)	33	12.4	- 178
3	CuDAS(P)	33	4.8	- 168

glacial acetic acid. Melting point : 152°C (literature melting point : 152°C).

(ii) Cobalt(II), Nickel(II), Copper(II), Iron(II), Manganese (II) and Lead(II) chelates of DNR: Metal salt (0.01 mole) dissolved in glacial acetic acid with few drops of water was added to 2:4-dinitroso resorcinol (0.01 mole) in glacial acetic acid with stirring and left overnight. The precipitates were filtered, washed with water and alcohol and dried at 70-80°C. These chelates were found insoluble in common organic solvents. Their analysis, magnetic susceptibility and electrical conductivity were determined and their IR spectra and thermograms (TGA) were obtained. The results are given in tables II.4(a) to (c) and figures II.4 (i) to (iii).

(iii) <u>Pyrolysis of chelates</u>: These chelates were pyrolyzed in miligram quantity in quartz tube with continuous evaccuation at 300-20°C. Some chelates like cobalt, lead were found explosive; so these were pyrolyzed with very little quantity of the initial products with precuations. The residue was washed with alcohol and acetone and dried. These were found insoluble in common organic solvents. Their analysis, magnetic susceptibility and IR spectra were obtained. The results are given in tables II.4(d) and (e) and figures II.4(iv).

TABLE II. 4(a)

Polychelates of 2,4-dinitrosoresorcinol (DNR)

melting point > 360° C

No	Metal in polychelates	Polychelate	Colour	Formula	Analysis (found)/(required) %C	% H	% M
1	Cobalt(II)	CoDNR	Brownish red	$CoC_6H_4N_2O_5$	30.7/29.6	1.5/1.6	23.1/24.2
2	Nickel(II)	NiDNR	dirty green	$NiC_6H_8N_2O_7$	26.3/25.8	3.0/2.9	20.8/21.1
3	Copper(II)	CuDNR	green	$CuC_6H_8N_2O_7$	25.2/25.4	3.0/2.8	23.0/22.4
4	Lead(II)	PbDNR	dirty green	$PbC_{12}H_6N_4O_8$	26.1/26.6	1.4/1.1	38.0/38.3
5	Iron(II)	FeDNR	dark green	$FeC_{12}H_8N_4O_9$	35.1/35.3	2.3/2.0	14.0/13.7

TABLE II.4(b)

Magnetic susceptibility of Polychelates of DNR

No	Polychelates	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
1	CoDNR	32	5.9	- 75
2	NiDNR	32	13.9	- 96
3	CuDNR	32	Diam	-
4	FeDNR	32	19.9	- 136
5	PbDNR	32	Diam	-

TABLE II.4(c)

Solid State Electrical Resistance of Polychelates of DNR

No	Polychelate	Resistance of pellet R (ohms) $\times 10^{-9}$	Thickness/area of pellet l/a (cm^{-1})	Temperature (°C)
1	CoDNR	36	0.4502	28
2	NiDNR	190	0.2353	28
3	CuDNR	850	0.2711	28
4	MnDNR	400	0.2372	28
5	FeDNR	30	0.3495	28
6	PbDNR	700	0.2585	28

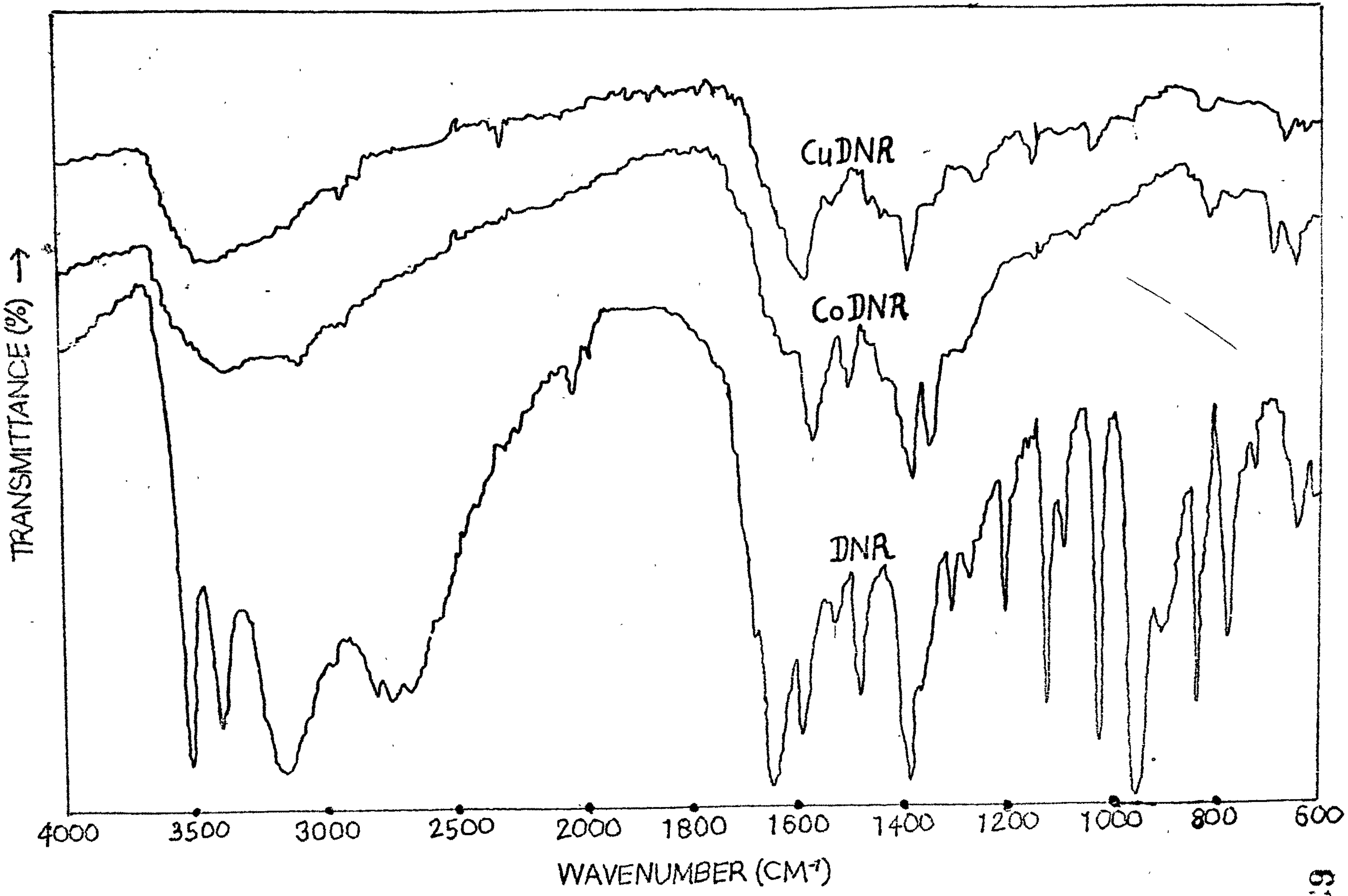

Fig. II 4 (i) IR spectra of DNR, CuDNR and CoDNR

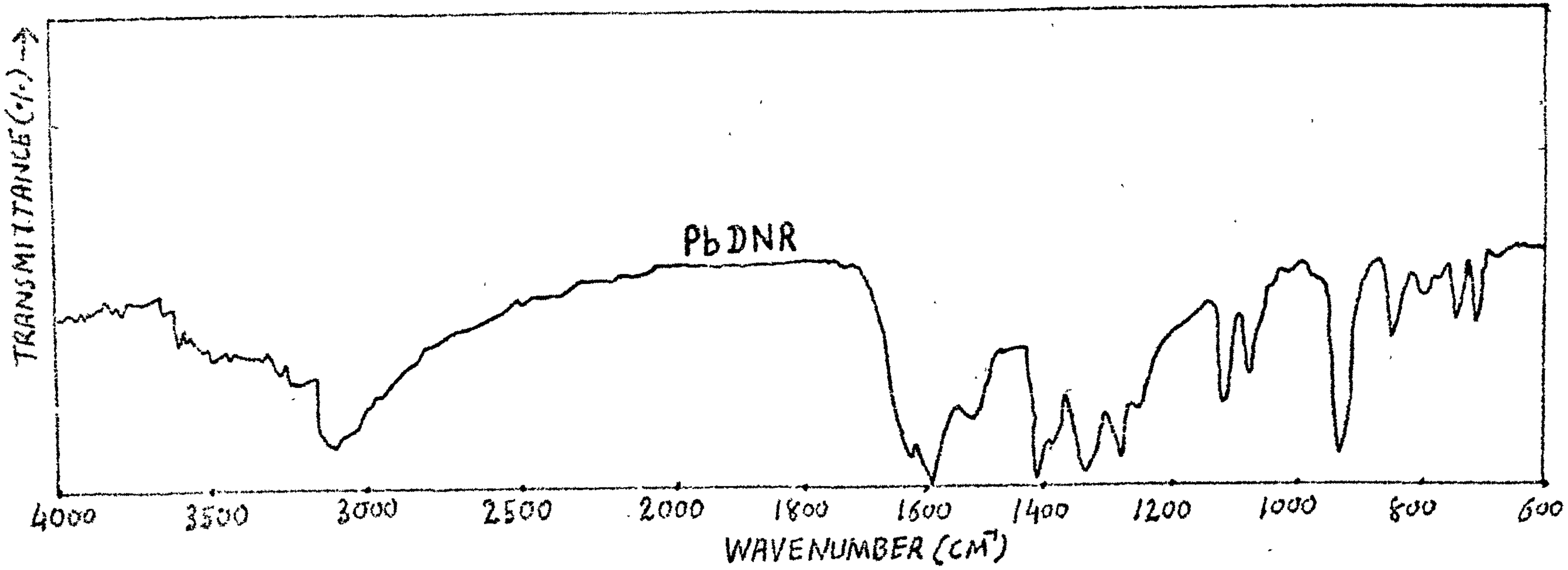

Fig. II.4 (ii). IR spectra of PbDNR

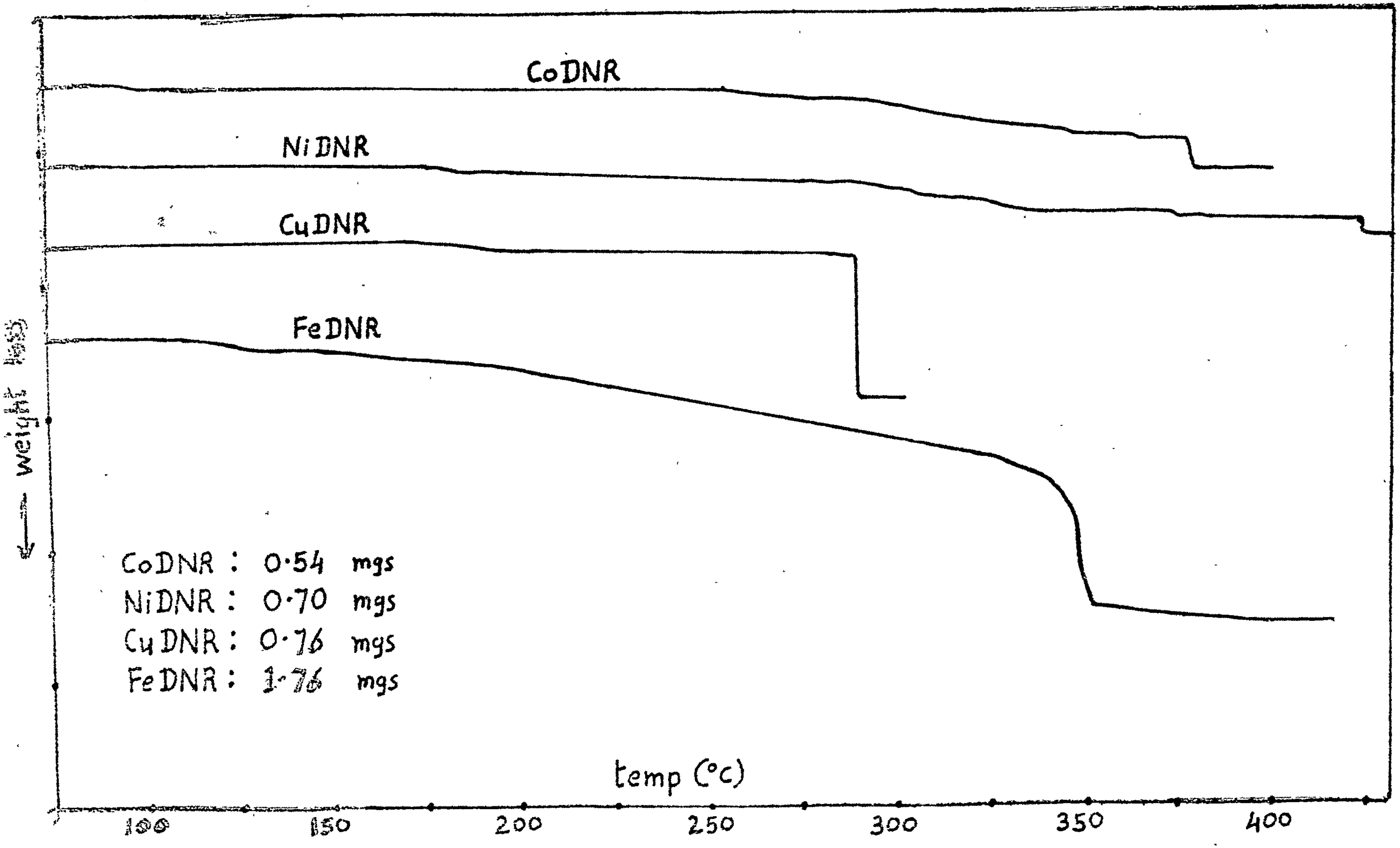

Fig.II.4(iii) TGA curves of CoDNR, NiDNR, CuDNR and FeDNR

TABLE II.4(d)

Pyrolyzed polychelates of DNR
(temperature of pyrolysis : 300–320°C)
melting point: > 360°C

No	Metal in polychelate	Polychelate	Colour	Formula	analysis (found)/(required) % N	% M
1	Co	CoDNR(P)	black	$CoC_6N_2O_4$	$\frac{12.8}{12.5}$	$\frac{26.4}{26.4}$
2	Ni	NiDNR(P)	black	$NiC_6N_2O_4$	$\frac{12.7}{12.6}$	$\frac{26.0}{26.4}$
3	Cu	CuDNR(P)	black	$Cu_2C_6N_2O_5$	$\frac{9.2}{9.1}$	$\frac{41.3}{41.4}$

TABLE II.4(e)

Magnetic Susceptibility of Pyrolyzed Polychelates of DNR

No	Polychelates	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
1	CoDNR(P)	32	30	-79
2	NiDNR(P)	32	25	-79
3	CuDNR(P)	32	Diam	-

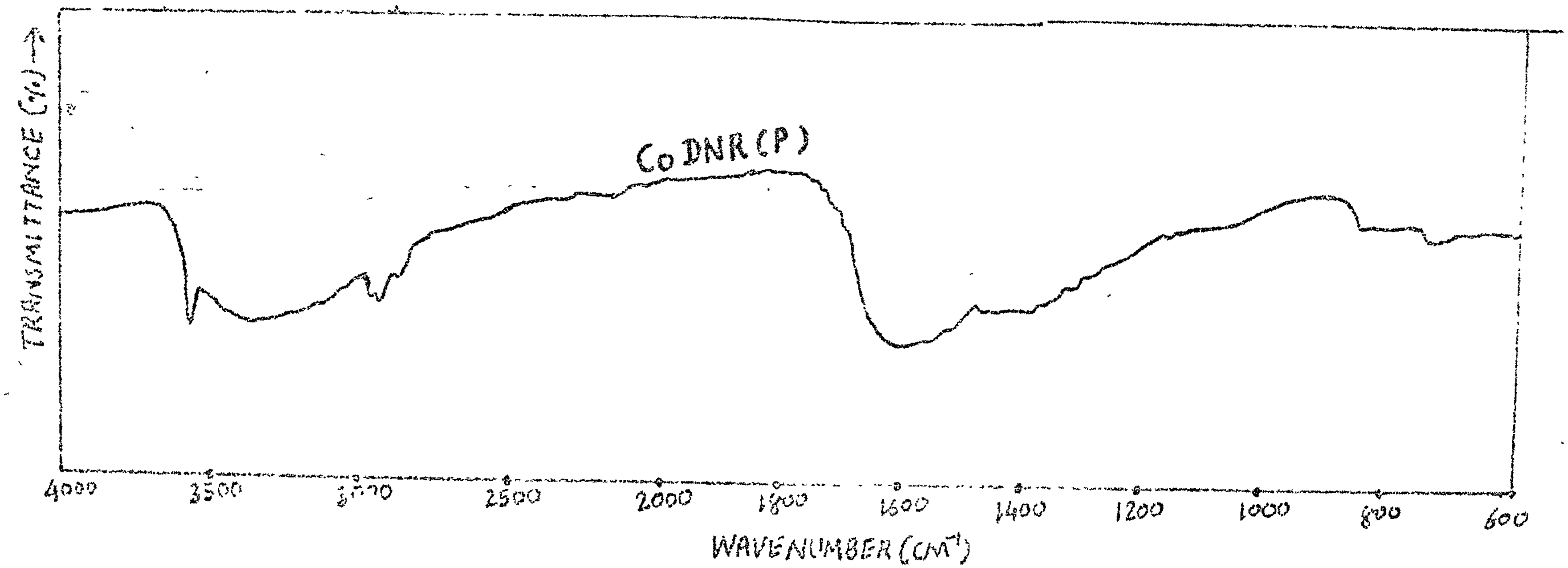

Fig. II.4 (iv) IR spectra of CoDNR(P)

II.5 Polychelates of (i) tetrazotized benzidine coupled with resorcinol (BAR) and (ii) tetrazotized 4,4'-diamino stilbene 2,2'-disulphonic acid coupled with resorcinol(SAR) and their pyrolysis

(i-a) Tetrazotized benzidine coupled with resorcinol

To the solution of 18.4gms of benzidine (0.1 mole) dissolved in 40 ml of conc. hydrochloric acid and 200 ml distilled water and cooled in ice bath to a temperature of 0 - 5°C was added the solution of 13.8 gms. sodium nitrite (0.2 mole) slowly with vigorous stirring, keeping the temperature of the mixture 0 - 5 °C. To this mixture, were added 40 gms of urea, the solution was stirred well and kept for one hour.

22 gms of resorcinol (0.2 mole) dissolved in a solution of 15 gms of sodium hydroxide in 200 ml distilled water, were taken in a flask, cooled in ice bath to maintain the temperature 0-5°C. To this solution was added the tetrazotized benzidine solution slowly with constant stirring maintaining the pH 9 to 10. The solution was then boiled to two-third of its volume, filtered and cooled. 20% hydrochloric acid solution was added as required when red precipitates were obtained. These were filtered, washed with hot water and alcohol, and dried at 70 - 80°C. The melting point of the compound is above 300°C.

Analysis :-

	Found	% C : 66.6	% H 4.2
$C_{24}H_{18}N_4O_4$	requires	% C: 67.6	% H 4.2

(i-b) Cobalt(II), Copper(II), Nickel(II), Manganese(II), Iron(II) and Lead(II) Polychelates of BAR in dimethyl formamide.

Ligand (0.01 mole) and metal acetate (0.01 mole) dissolved seperately in dimethyl formamide, were mixed slowly with stirring and kept overnight. They were refluxed on sand bath for two hours and cooled. The precipitates were filtered, washed with alcohol and acetone and dried at 100°C. The analysis, magnetic susceptibility, and electrical conductivity were determined and their IR spectra and thermograms (DTA and TGA) were obtained. The results are presented in tables II.5(a) to (c) and figures II 5(i),(ii),(iv), (v) and(vii).

(i-c) Pyrolysis of polychelates: These polychelates were pyrolyzed in quartz tube with continuous evaccuation at 410-430°C for one hour. The residual products were taken out of the tube, washed with alcohol and acetone and dried. The analysis, magnetic susceptibility, and IR spectra of these products were obtained and the results are given in tables II.5(d) and (e) and figures II.5(ii).

TABLE II.5(a)

(i) Polychelates of Tetrazotized benzidine coupled with Resorcinol (BAR) melting point $>$ 300°C

No	Metal in polychelate	Polychelate	Colour	Formula	Analysis % metal (found)/(required)	% N (found)/(required)
1	Cobalt(II)	CoBAR	reddish brown	$CoC_{24}H_{16}N_4O_4$	13.0/12.2	10.9/11.6
2	Nickel(II)	NiBAR	brown	$Ni_2C_{24}H_{22}N_4O_8$	18.9/19.2	9.4/9.2
3	Copper(II)	CuBAR	brown	$Cu_2C_{24}H_{28}N_4O_{11}$	18.5/18.8	8.5/8.3
4	Manganese(II)	MnBAR	brown	$Mn_2C_{24}H_{16}N_4O_5$	20.6/20.0	9.8/10.2
5	Iron(II)	FeBAR	brownish black	$Fe_2C_{24}H_{16}N_4O_5$	21.0/20.0	9.7/10.2
6	Lead(II)	PbBAR	brown	$PbC_{36}H_{25}N_6O_6$	25.9/25.4	6.5/6.9

TABLE II.5(a) (continued)

(ii) Polychelates of Tetrazotized 4,4'-diamino Stiline 2,2'-disulfonic Acid Coupled with Resorcinol (SAR)

M.P > 300°C

No	Metal in polychelate	Polychelate	Colour	Formula	Analysis % metal (found)/(required)	Analysis %N (Found)/(required)
1	Cobalt(II)	CoSAR	Shining reddish brown	$Co_3C_{26}H_{16}N_4O_{11}S_2$	22.3 / 22.1	7.4 / 7.0
2	Nickel(II)	NiSAR	Shining brown	$Ni_2C_{26}H_{16}N_4O_{10}S_2$	15.8 / 16.1	8.0 / 7.7
3	Copper(II)	CuSAR	shining brown	$Cu_2C_{26}H_{16}N_4O_{10}S_2$	17.5 / 17.3	7.9 / 7.6

TABLE II.5(b)

(i) Magnetic Susceptibility of Polychelates of BAR

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
1	CoBAR	32	22.0	- 246
2	NiBAR	32	15.2	- 147
3	CuBAR	32	2.8	- 163
4	MnBAR	32	45.7	- 131
5	FeBAR	32	42.9	- 131
6	PbBAR	32	Diam	-

TABLE II.5(b) (continued)

(ii) Magnetic Susceptibility of Polychelates of SAR

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
1	CoSAR	32	29.5	- 114
2	NiSAR	32	17.5	- 162
3	CuSAR	32	3.4	- 162

TABLE II. 5(c)

(i) Solid State Electrical Resistance of Polychelates of BAR

No	Polychelate	Resistance of pellet R (ohms)x10^{-9}	Thickness/area of pellet 1/a (cm^{-1})	Temperature (°C)
1	CuBAR	480	0.3215	28
2	CoBAR	600	0.2810	28
3	MnBAR	55	0.1975	28
4	FeBAR	4	0.2663	28
5	PbBAR	600	0.2614	28

TABLE II. 5(c) (continued)

(ii) Solid State Electrical Resistance of Polychelates of SAR

No	Polychelate	Resistance of pellet R (ohms) $x10^{-9}$	Thickness/area of pellet $l/a (cm^{-1})$	Temperature (°C)
1	CoSAR	15	0.3244	28
2	NiSAR	80	0.305	28
3	CuSAR	35	0.3098	28

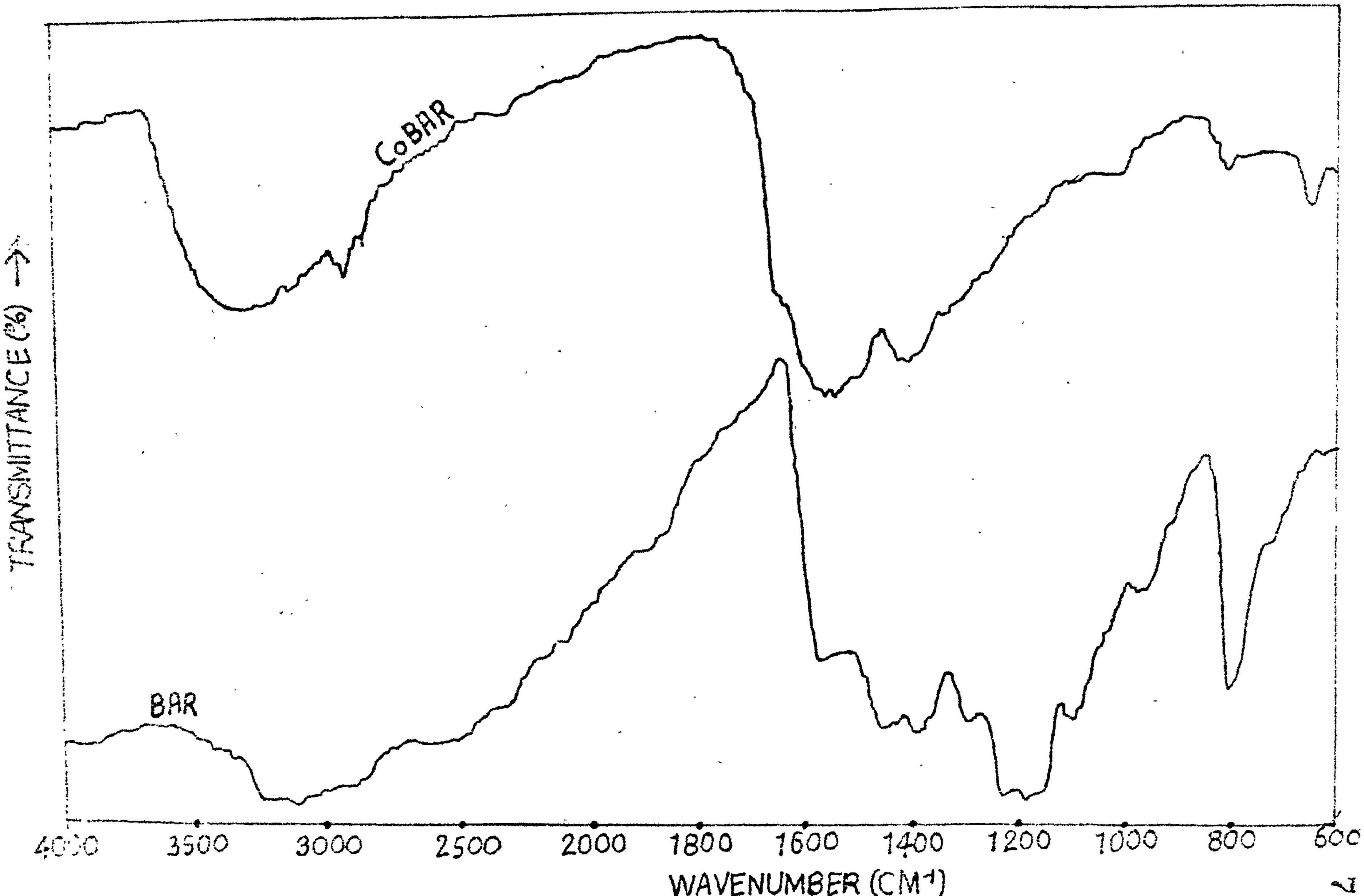

Fig. II.5 (i) IR spectra of CoBAR and BAR

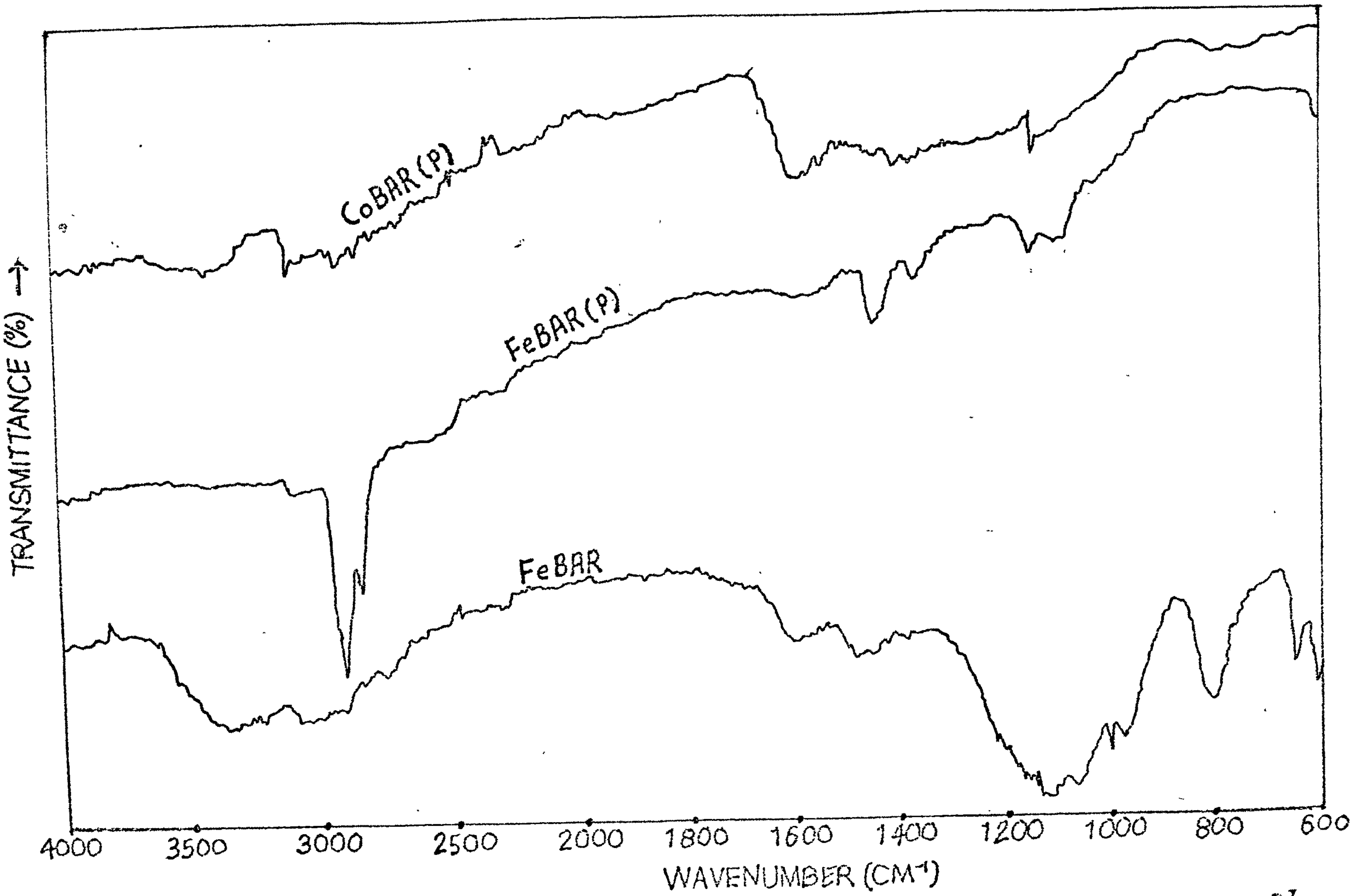

Fig. II.5 (ii). IR spectra of FeBAR, FeBAR(P), CoBAR(P)

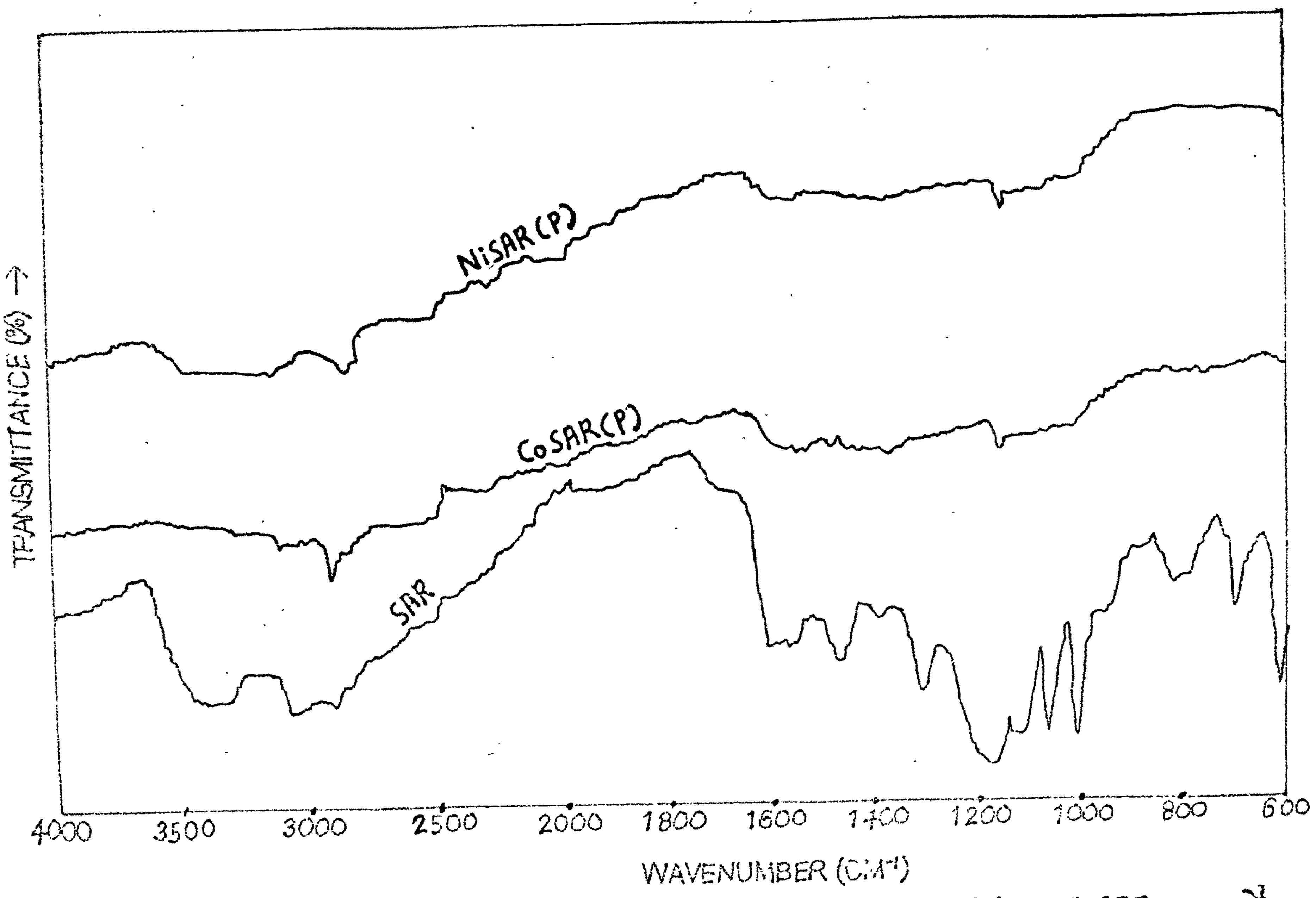

Fig. II.5 (iii) IR spectra of NiSAR(P), CoSAR(P) and SAR

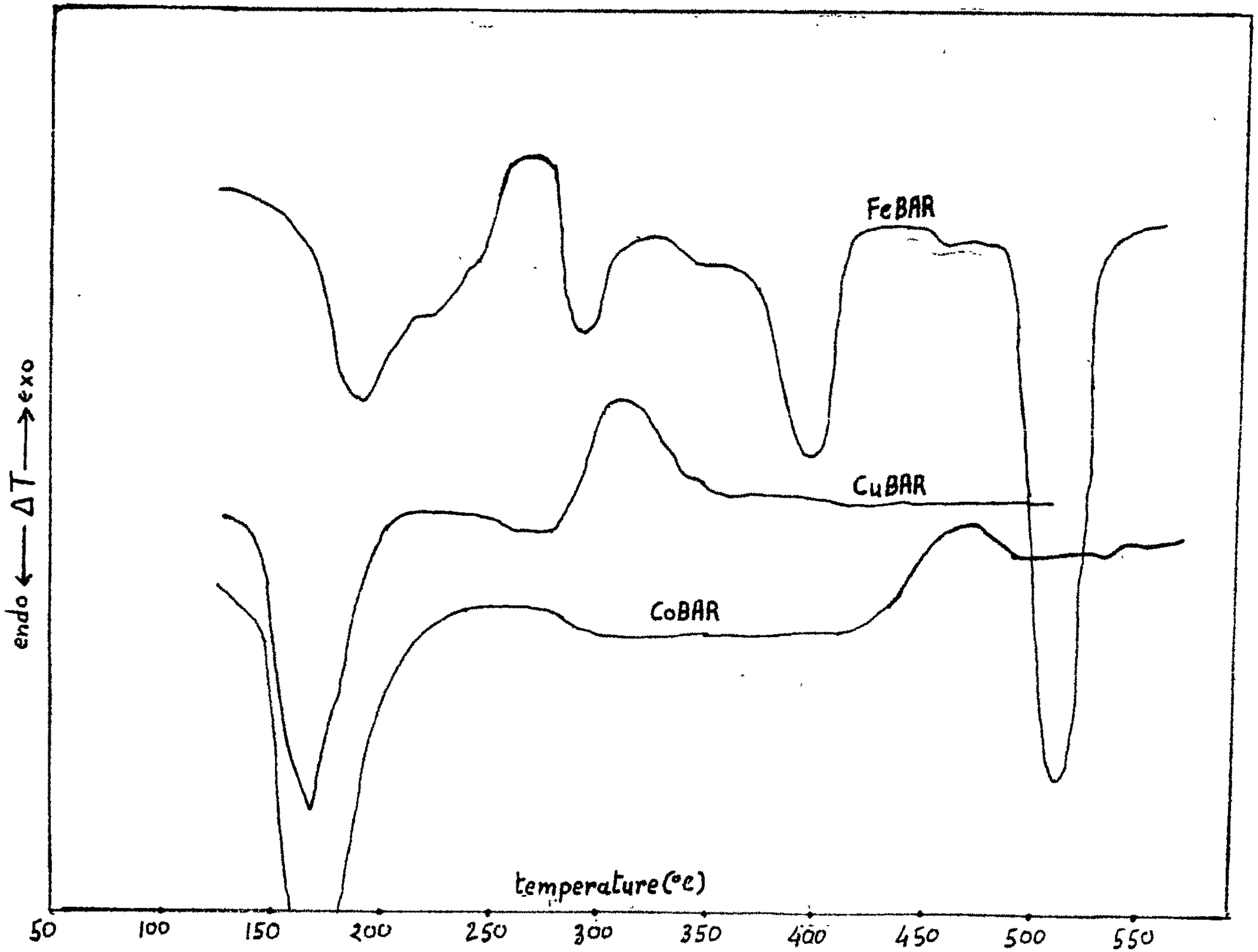

Fig. II.5(iv) DTA curves of FeBAR, CuBAR and CoBAR

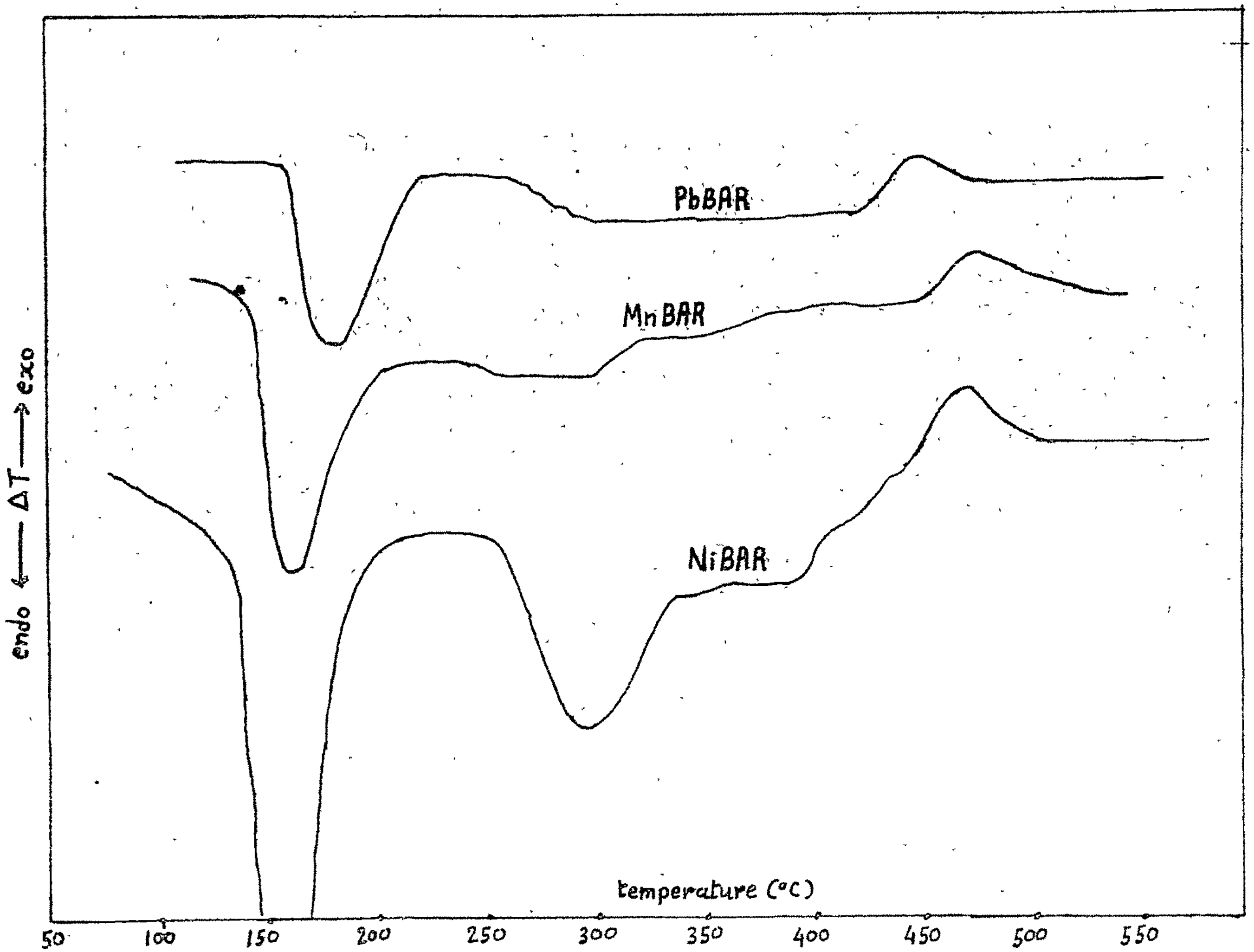

Fig.II.5(v) DTA curves of PbBAR, MnBAR and NiBAR

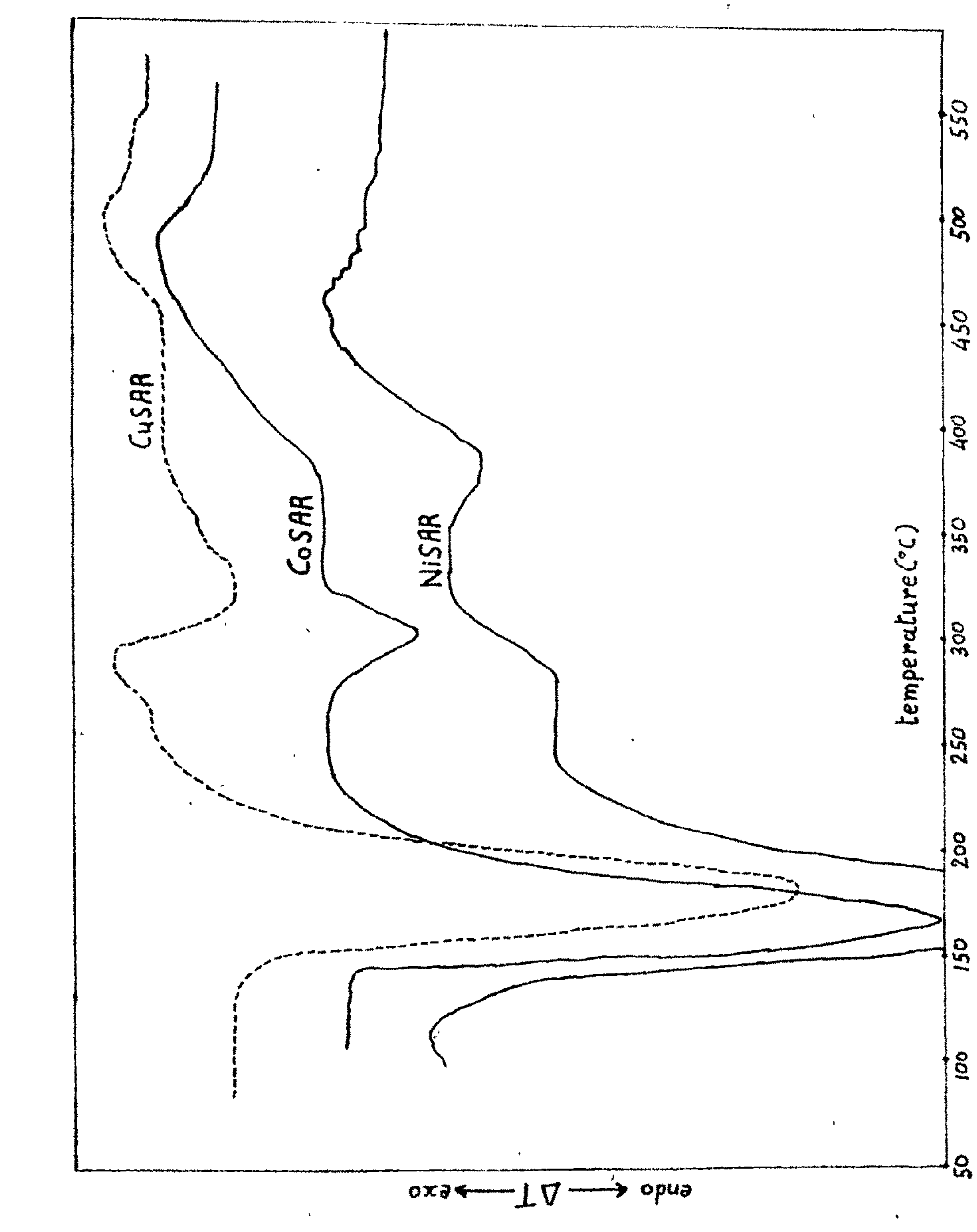

Fig.II.5(vi) DTA curves of CuSAR, CoSAR and NiSAR

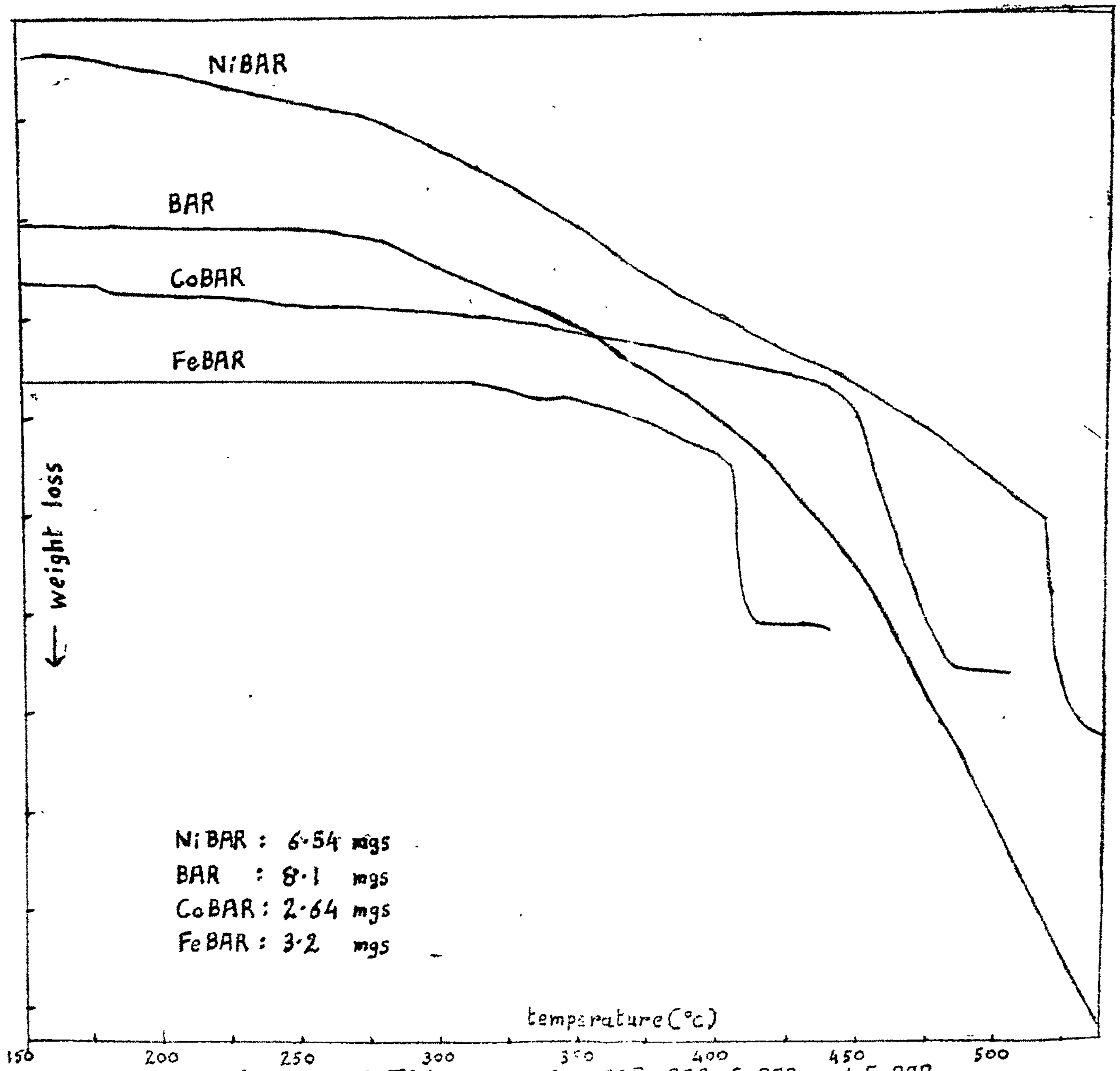

Fig. II.5 (vii) TGA curves of NiBAR, BAR, CoBAR, and FeBAR

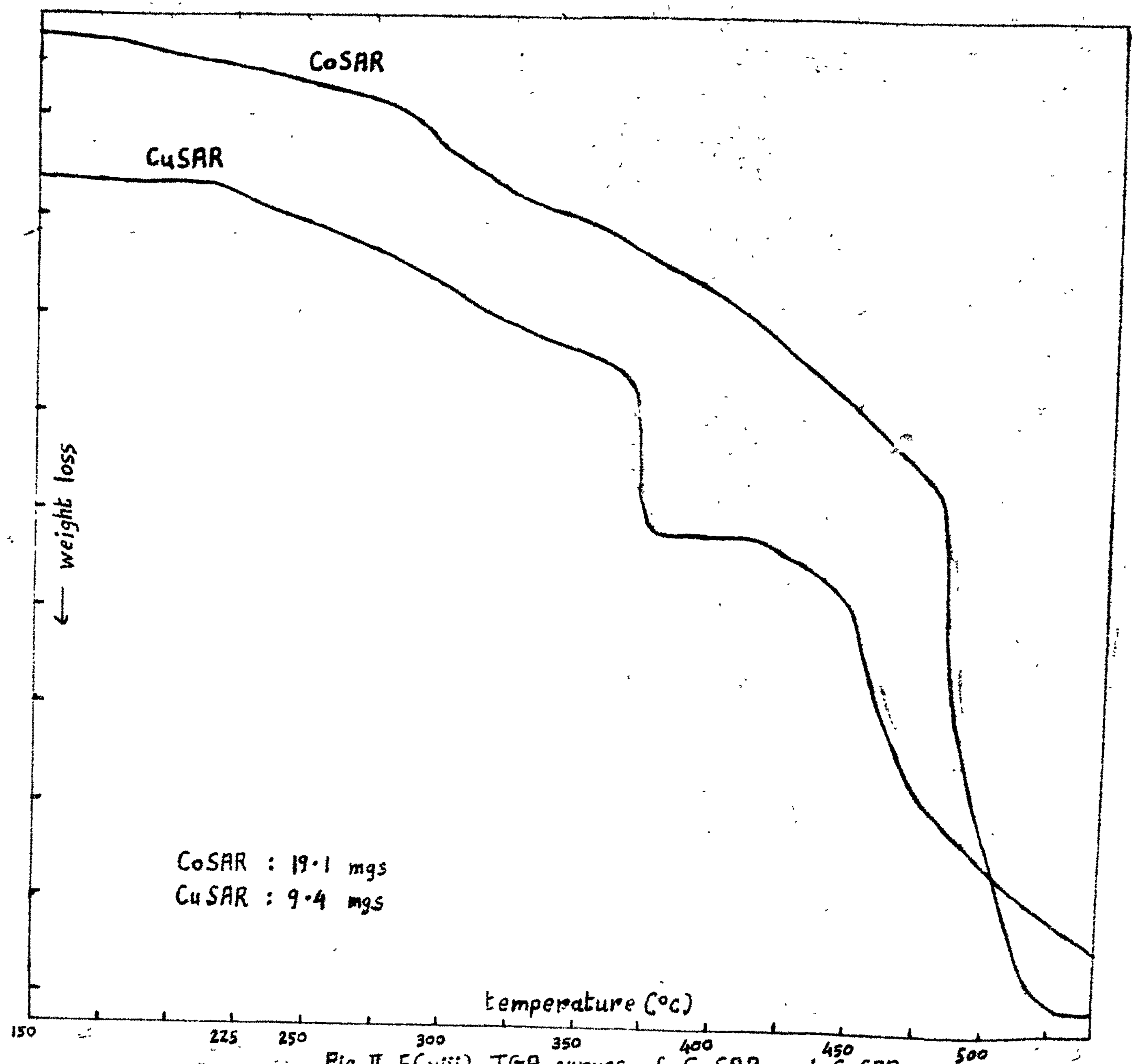

Fig. II. 5(viii) TGA curves of CoSAR and CuSAR

TABLE II. 5(d)

(i) Pyrolyzed Polychelates of BAR (temperature of Pyrolysis 410-30°C)

No	Metal in Polychelate	Polychelate	Colour	Formula	Analysis %metal (found)/(required)	% N (found)/(required)
1	Cobalt(II)	*CoBAR(P)	black	$CoC_{24}H_{12}N_2O_4$	14.1/13.1	5.8/6.2
2	Nickel(II)	NiBAR(P)	black	$Ni_2C_{24}H_{12}N_2O_5$	22.0/22.3	5.9/5.3
3	Copper(II)	CuBAR(P)	black	$Cu_2C_{24}H_{12}N_2O_5$	24.0/23.7	5.8/5.2
4	Manganese(II)	MnBAR(P)	black	$Mn_2C_{24}H_{12}N_2O_5$	19.9/21.2	5.7/5.4
5	Iron(II)	*FeBAR(P)	black	$Fe_2C_{24}H_{12}N_2O_5$	21.0/21.5	5.8/5.4

TABLE II.5(d) (continued)

(ii) Pyrolyzed Polychelates of SAR
(pyrolyzed at 410–30°C)

No	Metal in Polychelate	Polychelate	Colour	Formula	Analysis %metal (found)/(required)	% N (found)/(required)
1	Cobalt(II)	*CoSAR(P)	black	$Co_3C_{26}H_{16}N_3O_{11}S_2$	22.9/22.5	5.8/5.3
2	Nickel(II)	*NiSAR(P)	black	$Ni_2C_{26}H_{16}N_3O_{10}S_2$	17.0/16.5	6.3/5.9
3	Copper(II)	CuSAR(P)	black	$Cu_2C_{26}H_{16}N_3O_{10}S_2$	18.5/17.5	5.8/5.8

TABLE II.5(e)

(i) Magnetic Susceptibility of Pyrolyzed Polychelates of BAR

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility X_g x10^6	Diamagnetic correction (per metal ion) x10^6
1	*CoBAR(P)	30	-F	-
2	NiBAR(P)	30	10.5	-121
3	CuBAR(P)	30	2.6	-121
4	MnBAR(P)	30	45.7	-121
5	*FeBAR(P)	30	-F	-

TABLE II.5(e) (continued)

(ii) Magnetic Susceptibility of Pyrolyzed Polychelates of SAR

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility X_g x10^6	Diamagnetic correction (per metal ion) x10^6
1	*CoSAR(P)	33	F	-
2	*NiSAR(P)	33	F	-
3	CuSAR(P)	33	4.0	160

(ii-a) Tetrazotized 4:4'-diamino stilbene 2:2'-disulfonic acid coupled with resorcinol (SAR):

To the solution of 38 gms of 4,4'-diamino stilbene-2,2'-disulfonic acid (0.1 mole) dissolved in 40 ml conc. hydrochloric acid and 200 ml distilled water, was added a solution of 13.8 gms sodium nitrite (0.2 mole) with constant stirring and maintaining the temperature 0-5°C. To this mixture, 40 gms urea were added and the mixture was kept for one hour.

22 gms of resorcinol (0.2 mole) dissolved in the solution of 15 gms sodium hydroxide in 200 ml water were taken in a flask and cooled to 0-5°C. The tetrazotized solution of benzidine was added slowly to the alkaline solution of resorcinol, with constant stirring, maintaining the pH 8-10. It was boiled to two-third its volume, cooled, and acidified with hydrochloric acid. To this solution was added saturated sodium chloride solution to get the precipitates. These were filtered, washed with water and little alcohol and dried at 70-80°C. The melting point of this compound is above 300°C.

Analysis :

	Found	% N	9.4
$C_{26}H_{20}N_4O_{10}S_2$	requires	% N	9.2

(ii-b) Cobalt(II), Nickel(II) and Copper Polychelates of SAR

Metal acetate (0.01 mole) and ligand (0.01 mole) dissolved seperately in liquor ammonia were mixed slowly with vigorous stirring. The mixture was left over night. The precipitates were filtered, washed with little ammonia, water and alcohol and dried at 70-80^{o}C. They were analysed and their magnetic susceptibility and electrical conductivity were determined and their IR spectra and thermograms (DTA and TGA) were obtained. The results are given in tables II.5(a) to (c) and figures II.5(iii),(vi) and (viii).

(ii-c) Pyrolysis of Polychelates:

These compounds were pyrolyzed at 410-430^{o}C in quartz tube under continuous evaccuation for one hour. The residual products were taken out of the tube, washed with alcohol and acetone and dried. The analysis, magnetic susceptibilities and IR spectra were studied. The results are given in tables II.5(d) and (e) and figure II.5 (iii)

II.6 Polychelates of (i) tetrazotized benzidine coupled with 2-hydroxy 3-Naphthoic acid (BAN) and (ii) tetrazotized 4,4'-diamino stilbene 2,2'-disulphonic acid coupled with 2-hydroxy 3-naphthoic acid (SAN) (i-a) <u>Tetrazotized benzidine coupled with 2-hydroxy 3-Naphthoic acid (BAN)</u>:

To the solution of 18.4 gms benzidine (0.1 mole) dissolved in 40 ml conc. hydrochloric acid and 200 ml distilled water and cooled in icebath to a temperature of 0-5^{o}C, was added the solution of 13.8 gms of sodium nitrite (0.2 mole) slowly, with constant stirring, keeping the temperature of the reaction mixture 0-5^{o}C. To this solution was added 40 gms Urea. The solution was stirred and kept in icebath for one year.

37.6 gms of 2-hydroxy 3-naphthoic acid (0.2 mole) dissolved in the solution of 30 gms sodium hydroxide in 200 ml distilled water was taken in a flask cooled to 0-5^{o}C. To this solution was added the solution of tetrazoitized benzidine slowly, with constant stirring, maintaining the pH 9-10. The mixture was boiled to two-third its original volume, cooled and to it was added 20% hydrochloric acid slowly to get the pH of the mixture 3-4 when precipitates were obtained. These were filtered, washed with hot water and alcohol and dried at 70-80^{o}C. The melting point of the compound is above 300^{o}C.

Analysis :-

	found	% C : 69.1	% H 4.0
$C_{34}H_{22}N_4O_6$	requires	% C : 70.1	% H 3.8

(i-b) Cobalt(II), Copper(II), Nickel(II) Polychelates of BAN in Dimethyl formamide:

Metal acetate (0.01 mole) and ligand (0.01 mole) dissolved seperately in dimethyl formamide were mixed slowly and kept overnight. They were refluxed on sand bath for three hours and cooled. The precipitates were filtered, washed with water and alcohol and dried at 70-80°C. The analysis, magnetic susceptibility, and electrical conductivity were determined and their IR spectra and thermograms (DTA and TGA) were obtained. The results are presented in tables II.6(a) to (c) and figures II.6 (i), (iii) and (v).

(i-c) Pyrolysis of Polychelates

All these compounds were pyrolyzed in quartz tube at 310-330°C under continuous evaccuation for one hour. The residual products were taken out and washed with alcohol and acetone and dried. The analysis, magnetic susceptibility and IR spectra were studied and the results are given in tables II.6 (d) and (e) and figure II.6 (i).

(ii-a) Tetrazotized 4,4'-diamino stilbene 2,2'-disulfonic acid coupled with 2-hydroxy 3-naphthoic acid (SAN)

38 gms 4,4'-diamino stilbene 2,2'-disulfonic acid (0.1 mole) were dissolved in 40 ml conc. hydrochloric acid

TABLE II.6(a)

(i) Polychelates of Tetrazotized benzidine Coupled with 2-hydroxy 3-naphthoic acid (BAN)

melting point > 300°C

No	Metal in Polychelates	Polychelate	Colour	Formula	Analysis % metal (found)/(required)	%N (found)/(required)
1	Cobalt(II)	CoBAN	reddish brown	$CoC_{34}H_{20}N_4O_6$	9.1 / 9.2	9.1 / 8.8
2	Copper(II)	CuBAN	brown	$CuC_{34}H_{20}N_4O_6$	9.6 / 9.9	8.8 / 8.7

TABLE II.6(a) (continued)

(ii) Polychelates of Tetrazotized 4,4'-diamino stilbene 2,2'-disulfonic acid Coupled with 2-hydroxy 3-naphthoic acid (SAN)

melting point: $>$ 300°C

No	Metal in polychelate	Polychelate	Colour	Formula	Analysis % metal (found)/(required)	Analysis % N (found)/(required)
1	Cobalt(II)	CoSAN	Shining brownish black	$Co_2C_{36}H_{18}N_4O_{12}S_2$	14.1 / 13.4	5.8 / 6.4
2	Nickel(II)	NiSAN	shining brown	$Ni_4C_{40}H_{30}N_4O_{20}S_2$	18.9 / 19.8	4.8 / 4.7
3	Copper(II)	CuSAN	shining brown	$Cu_3C_{36}H_{16}N_4O_{12}S_2$	20.0 / 20.0	6.1 / 5.9

TABLE II.6(b)

Magnetic Susceptibility of Polychelates

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility X_g x10^6	Diamagnetic correction (per metal ion) x 10^6
	(i) Polychelates of BAN			
1	CoBAN	32	22.8	- 337
2	CuBAN	32	3.0	- 337
	(ii) Polychelates of SAN			
3	CoSAN	32	25.6	- 207
4	NiSAN	32	15.8	- 133
5	CuSAN	32	4.0	- 140

TABLE II.6(c)

Solid State Electrical Resistance of Polychelates

No &	Polychelate	Resistance of pellet R (ohms)x10^{-9}	Thickness/area of pellet 1/a (cm^{-1})	Temperature (°C)
	(i) Polychelates of BAN			
1	CuBAN	35	0.2517	28
2	CoBAN	500	0.3563	28
	(ii) Polychelates of SAN			
3	CoSAN	300	0.3340	28
4	NiSAN	55	0.3340	28
5	CuSA	170	0.3137	28

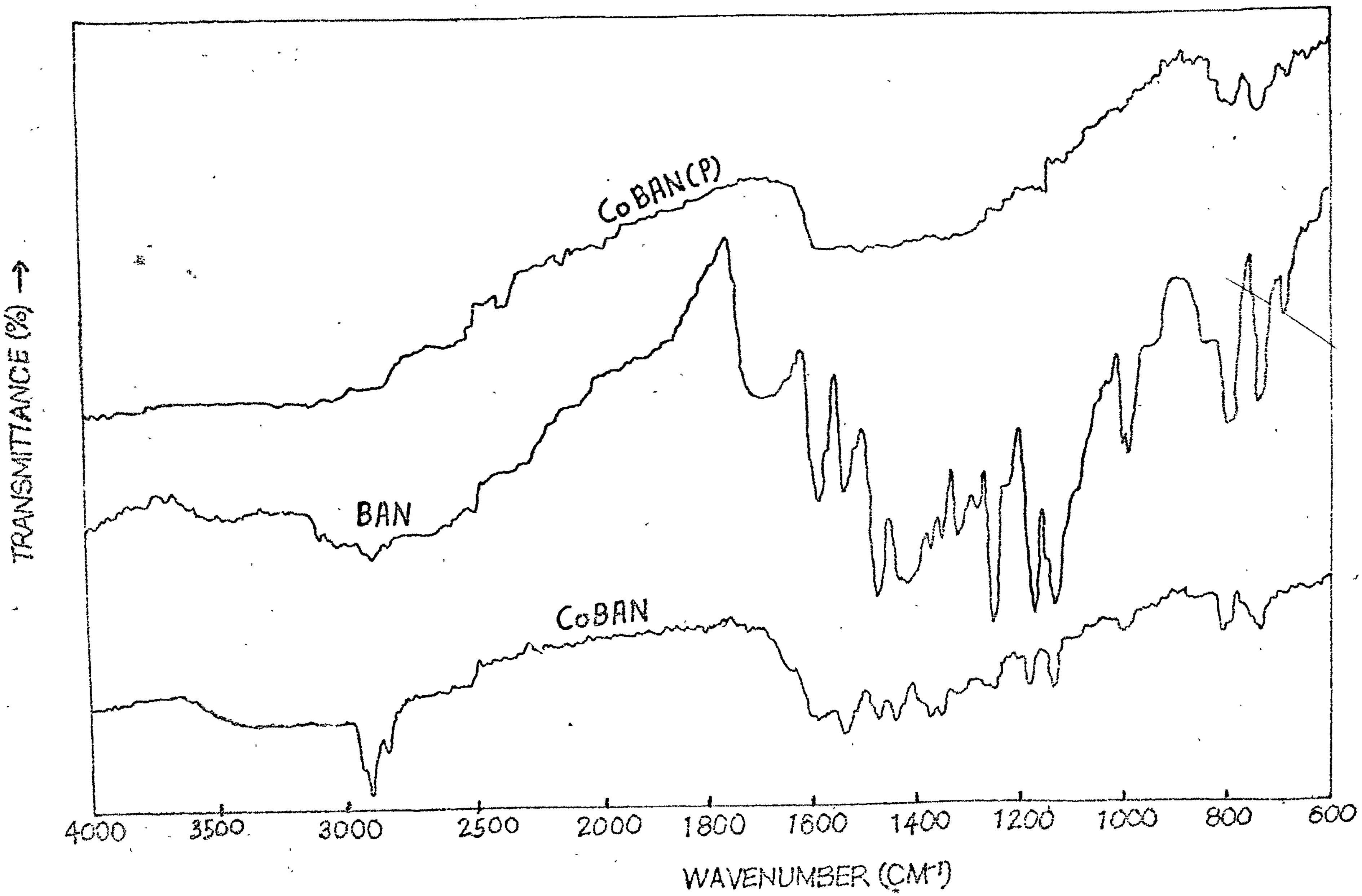

Fig. II.6.(i) IR spectra of BAN, CoBAN and CoBAN(P)

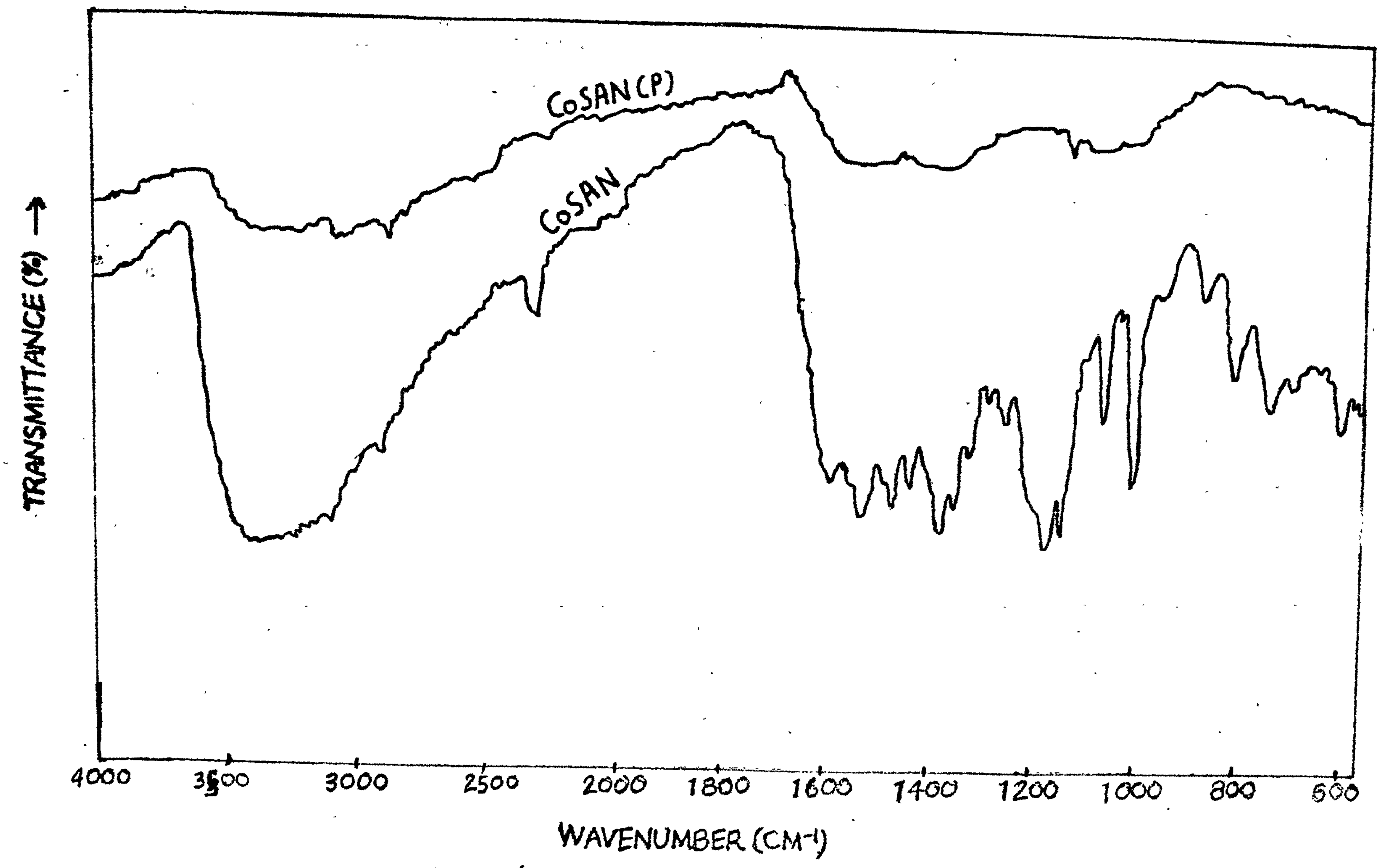

Fig. II.6.(ii) IR spectra of CoSAN and CoSAN(P)

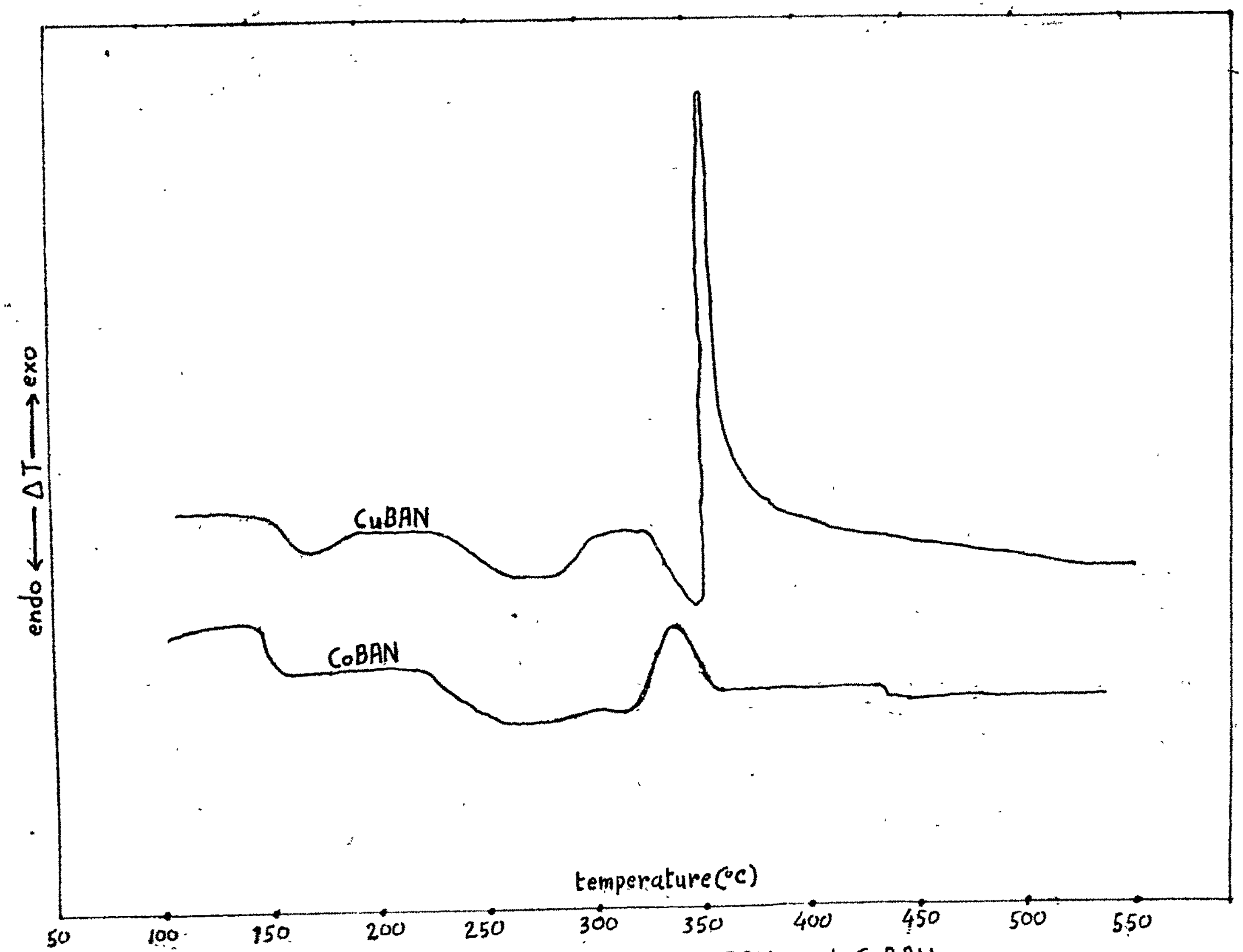

Fig. II.6(iii) DTA curves of CoBAN and CuBAN

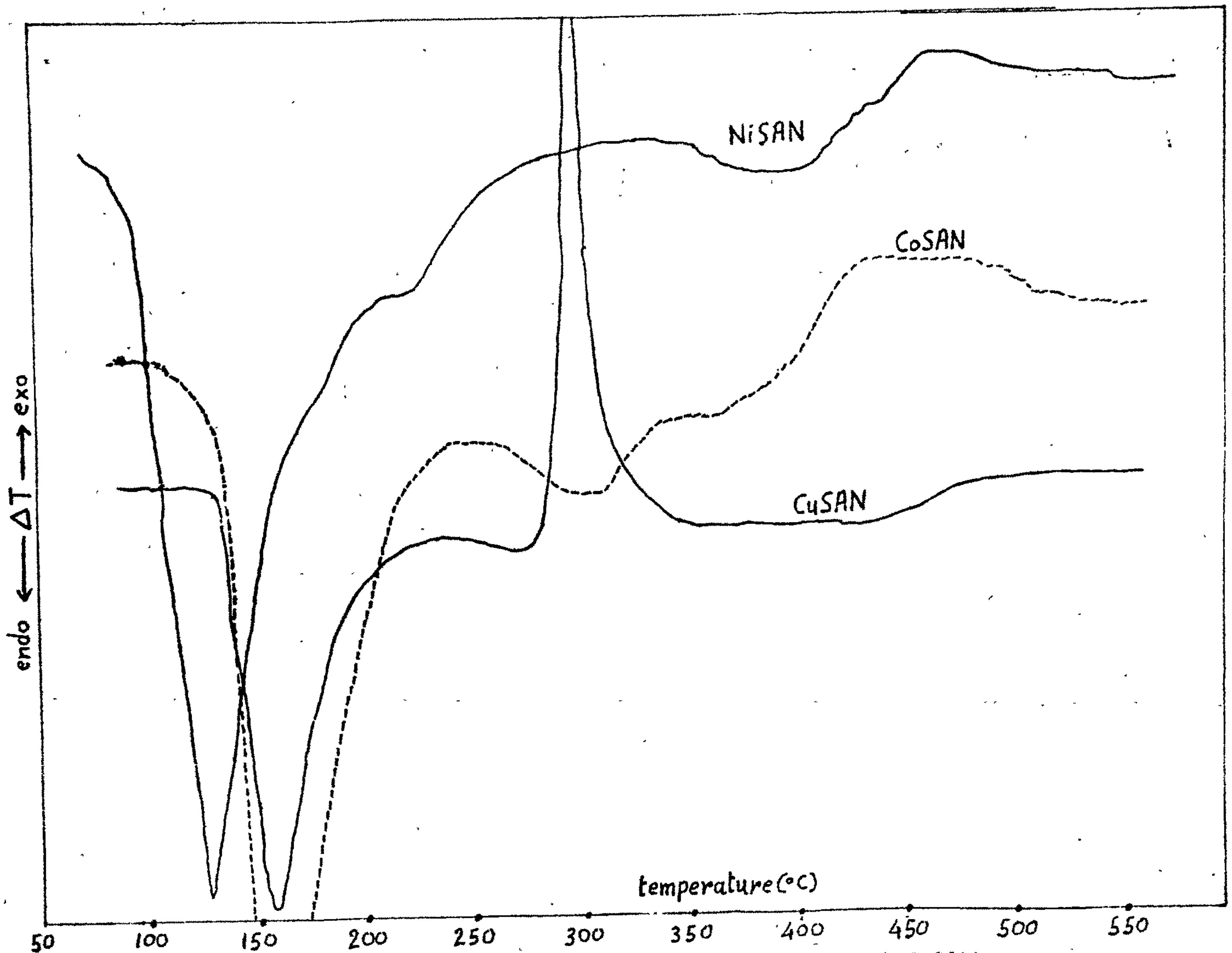

Fig. II.6(iv) DTA curves of NiSAN, CoSAN and CuSAN

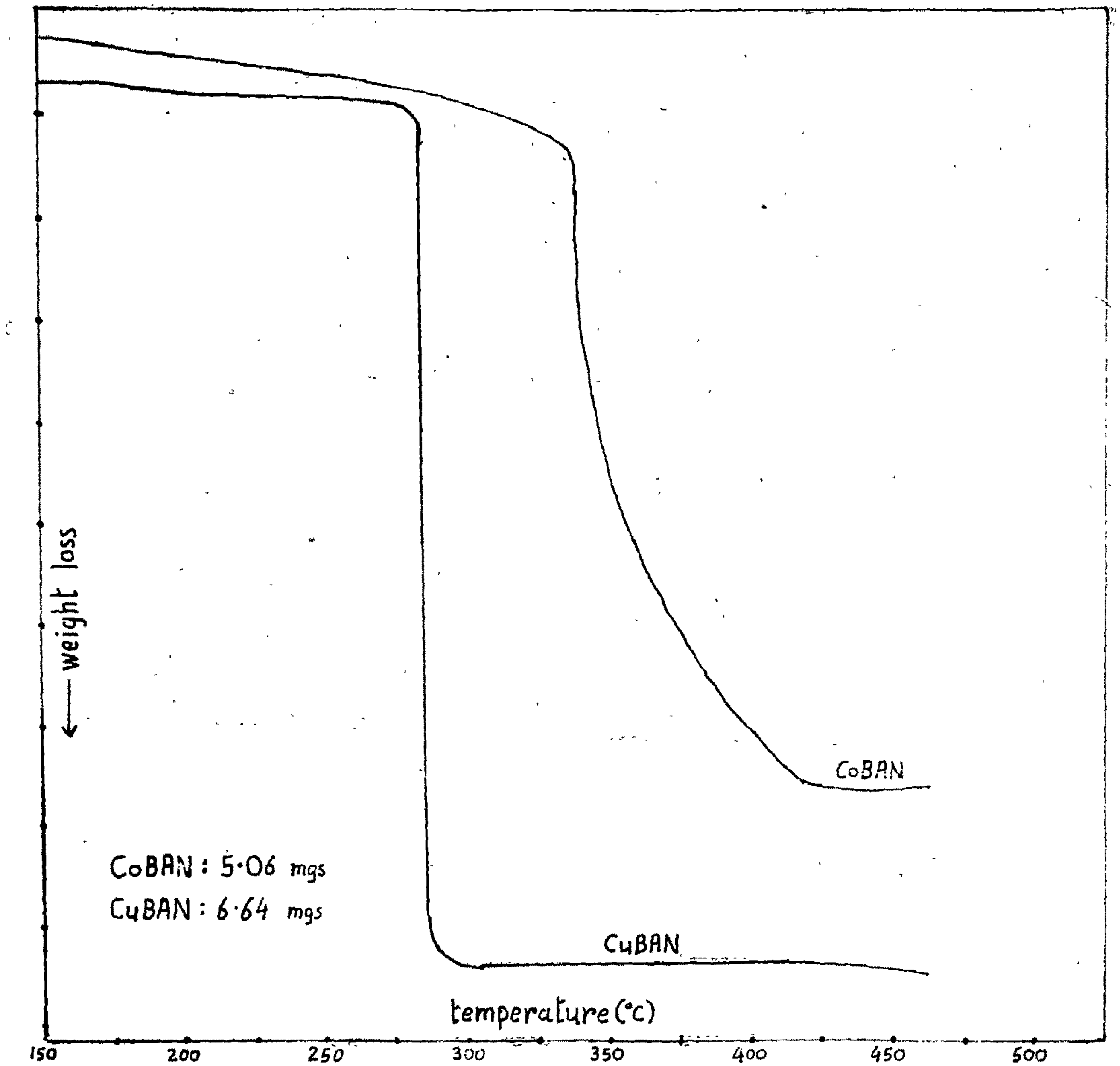

Fig. II.5 (v). TGA curves of CoBAN and CuBAN

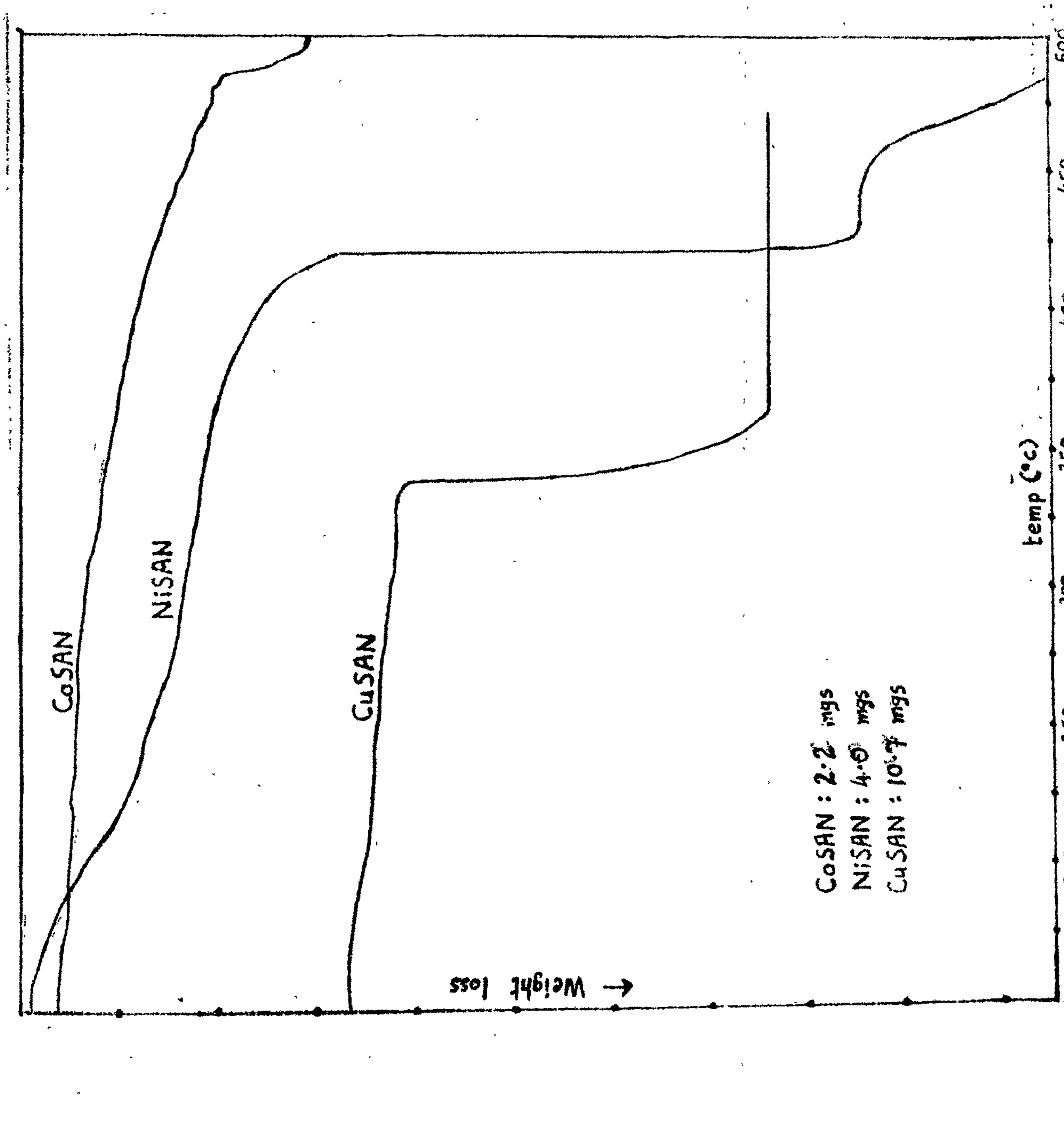

Fig. II 6(vi) TGA curves of CoSAN, NiSAN and CuSAN

TABLE II.6(d)

(i) Pyrolyzed Polychelates of Tetraazotized benzidine Coupled with 2,hydroxy 3,naphthoic acid (pyrolyzed at 310-30°C)

No	Metal in polychelate	Polychelate	Colour	Formula	Analysis: % metal (Found)/(required)	Analysis: % N (found)/(required)
1	Cobalt	*CoBAN(P)	black	$CoC_{33}H_{20}N_2O_4$	10.4 / 10.4	4.2 / 4.9
2	Copper	CuBAN(P)	black	$CuC_{33}H_{20}N_2O_4$	10.6 / 11.1	4.7 / 4.9

TABLE II.6(d) (continued)

(ii) Pyrolyzed polychelates of tetraazotized 4,4'-diamino stilbene disulfonic acid coupled with 2-hydroxy 3-naphthoic acid (pyrolyzed at 310-30°C)

No	Metal in	Polychelate	Colour	Formula	Analysis % metal (found)/(required)	% N (found)/(required)
1	Cobalt	* CoSAN(P)	black	$Co_2C_{35}H_{20}N_2O_{10}S_2$	14.5/14.5	3.5/3.4
2	Nickel	* NiSAN(P)	black	$Ni_4C_{35}H_{18}N_2O_{12}S_2$	24.8/25.0	2.5/3.0
3	Copper	CuSAN(P)	black	$Cu_3C_{35}H_{18}N_2O_{11}S_2$	21.1/21.2	2.9/3.1

TABLE II.6(e)

Magnetic susceptibility of pyrolyzed polychelates

No	Polychelate	Temperature (°C)	Magnetic mass susceptibility $X_g \times 10^6$	Diamagnetic correction (per metal ion) $\times 10^6$
	(i) Pyrolyzed polychelates of BAN			
1	* CoBAN(P)	33	F	-
2	CuBAN(P)	33	3.9	-328
	(ii) Pyrolyzed polychelates of SAN			
3	* CoSAN(P)	32	F	-
4	* NiSAN(P)	32	F	-
5	CuSAN(P)	32	4.8	-138

and 200 ml distilled water and cooled to 0-5°C in icebath. To this solution was added a solution of 13.8 gms sodium nitrite (0.2 mole) slowly, with constant stirring, maintaining the temperature 0-5°C and finally 40 gms Urea were added. This mixture was left for one hour.

37.6 gms 2-hydroxy 3-naphthoic acid (0.2 mole) were dissolved in sodium hydroxide solution and cooled to 0-5°C in ice bath. To this solution was added tetrazotized solution slowly, with constant stirring, maintaining the pH 8-10. This mixture was boiled to half its volume and was acidified with hydrochloric acid and precipitated by addition of saturated sodium chloride solution. The precipitates were filtered, washed with water and alcohol and dried. The compound does not melt upto 360°C.

Analysis

	found	% C : 56.8	% H 3.0
$C_{36}H_{22}N_4O_{12}S_2$	requires	% C : 56.4	% H 3.0

(ii-b) Cobalt(II), Copper(II), Nickel(II) Polychelates of SAN

Metal acetate (0.01 mole) and ligand (0.01 mole), dissolved seperately in liquor ammonia, were mixed slowly with constant stirring and left overnight. The precipitates were filtered, washed with ammonia and alcohol and dried.

The analysis, magnetic susceptibility and electrical conductivity were determined and their IR spectra and thermograms (DTA and TGA) were studied. The observations are presented in tables II.6(a) to (c) and figures II.6 (ii), (iv) and(vi).

(ii-c) Pyrolysis of Polychelates:

These compounds were then pyrolyzed at 310-330°C in quartz tube under vacuum for one hour. The residual products were taken out of the tube, washed with alcohol and acetone, and dried.

These were analysed and their magnetic susceptibilities and IR spectra were obtained. The results are given in tables II.6 (d) and (e) and figure II.6(ii).