3 Experimental and Results

3.1 Qualitative study of the effect of ligands on nickel and cobalt-bentonite

3.1.1 Preparation of samples of bentonite

For this experiment, bentonite which is a type of clay in montmorillonite group was reacted with nickel and cobalt. Nickel and cobalt sorbed on the surface of the clay. because this clay has important property called "sorption property" of metal ions on clay.

procedure

Sample of bentonite 15 g were shaken with 0.1M solution of $NiCl_2$ or $CoCl_2$ (150 ml) for 3 days, filtered and left to air-dry. The clays were then resuspended in distilled water (150 ml) and shaken for a further 3 days, filtered and air-dried. The washing procedure was repeated and the air-dried clays were crushed to a fine powder prior to use in the following experiments. This clay samples were called Ni-bentonite and Co-bentonite, respectively.

Portion of each clay samples 1 g was digested by nitric aqua regia. A quantitative analysis of nickel and cobalt in Ni-bentonite and Co-bentonite were carried out by using Atomic absorption spectrophotometry.

3.1.2 Result of Atomic absorption spectrophotometry

Clay, untreated with $NiCl_2$ and $CoCl_2$ solution contained
nickel 4.22×10^{-3} mmole/g and
cobalt 3.17×10^{-3} mmole/g.

Nickel-bentonite clay sample contained
nickel 2.25 mmole/g.

Cobalt-bentonite clay sample contained
cobalt 2.10 mmole/g.

3.1.3 Treatment of Ni (Co) clay with ligands

Ligands were ammonia(NH_3), 1,2-diaminoethane (ethylene-diamine, en), dimethylglyoxime(DMG) and 2,2'-bipyridyl(bipy).

Procedure

Samples (2 g /4.5 mmole Ni^{2+}; 2 g /4.2 mmole Co^{2+}) of the above treated clays were contacted with ligands.

Ni-bentonite and Co-bentonite were treated with NH_3 solution. Various ratio of
Ni/NH_3 was 1 : 3, 1 : 10 and 1 : 25 and
Co/NH_3 was 1 : 3, 1 : 10 and 1 : 25.
Then clay samples were cooled in running water. Fine crystals were compleated by addition of an ammonical NH_4Cl solution. The mixture was stirred for 4 h. The solids were filtered, air-dried and subjected to Infrared spectrophotometry and Diffuse reflectance analysis. The filtrate solution was examined by UV-vis spectrophotometry.

Ni-bentonite and Co-bentonite were treated with en solution. Various ratio of

Ni /en was 1 : 1 and 1 : 9 and
Co /en was 1 : 1 and 1 : 9.

The mixture was stirred for 4 h. The solids were filtered, air-dried and subjected to Infrared spectrophotometry and Diffuse reflectance analysis. The filtrate solution was examined by UV-vis spectrophotometry.

Ni-bentonite and Co-bentonite were treated with DMG solution. Ratio of

Ni /DMG was 1 : 6 and
Co /DMG was 1 : 6.

The mixture was stirred for 4 h. The solids were filtered, air-dried and subjected to Infrared spectrophotometry and Diffuse reflectance analysis. The filtrate solution was examined by UV-vis spectrophotometry.

Ni-bentonite and Co-bentonite were treated with bipy solution. Ratio of

Ni /bipy was 1 : 5 and
Co /bipy was 1 : 5.

The mixture was stirred for 4 h. The solids were filtered, air-dried and subjected to Infrared spectrophotometry and Diffuse reflectance analysis. The filtrate solution was examined by UV-vis spectrophotometry.

3.1.4 Colour of clay samples

Colour of nickel compounds and cobalt compounds on clay samples obtained from treated Ni-bentonite and Co-bentonite with organic ligands was shown in Table. 3.1.

Table 3.1 Colour of nickel compounds and cobalt compounds

organic ligand added	metal / ligand ratio	colour of solid		colour of solution	
		nickel	cobalt	nickel	cobalt
NH_3	1: 3	green	pink	green	orange
NH_3	1: 10	green	pink	green	orange
NH_3	1: 25	green	pink	green	orange
en	1: 1	brown	brown	brown	brown
en	1: 9	brown	orange	brown	brown
DMG	1: 6	violet	brown	-	green
bipy	1: 5	pink	pink	-	-

note: - means no colour or clear

3.1.5 Infrared spectrum

The solid of each nickel compounds and cobalt compounds on clay sample was scannined in the infrared region and its spectrum was recorded by KBr disc method.

Infrared spectra of nickel and cobalt compounds on clay were tabulated in Table 3.2-3.9.

Table 3.2 Infrared spectrum of Ni : NH_3 at various ratio 1 : 3, 1 : 10 and 1 : 25

Substance	Wavenumber (cm^{-1})	Assignments
Ni : NH_3 1 : 3	3150 (br) 3000 (m) 1650 (s-m) 1370 (s-m)	$\nu_a(NH_3)$ $\nu_s(NH_3)$ $\delta_a(HNH)$ $\delta_s(HNH)$
Ni : NH_3 1 : 10	3150 (br) 3000 (m) 1650 (m-w) 1380 (m-w)	$\nu_a(NH_3)$ $\nu_s(NH_3)$ $\delta_a(HNH)$ $\delta_s(HNH)$
Ni : NH_3 1 : 25	3150 (br) 3000 (m) 1650 (w) 1400 (w)	$\nu_a(NH_3)$ $\nu_s(NH_3)$ $\delta_a(HNH)$ $\delta_s(HNH)$

Table 3.3 Infrared spectrum of Ni : en at various ratio 1 : 1 and 1 : 9

Substance	Wavenumber (cm^{-1})	Assignments
Ni : en 1 : 1	2970 (vw) 2880 (vw) 1650 (m)	$\nu_s(CH_2)$ $\delta_a(HNH)$
Ni :en 1 : 9	2940 (vw) 2880 (vw) 1600 (w) 1500 (w) 1350 (vw)	$\nu_s(CH_2)$ $\delta_a(HNH)$ $\delta_a(HNH)$ $\delta_s(HNH)$

Table 3.4 Infrared spectrum of Ni : DMG at ratio 1 : 6

Substance	Wavenumber (cm^{-1})	Assignments
Ni : DMG 1 : 6	3050 (vw)	ν(OH)
	1550 (w)	ν_{as}(NO)
	1420 (w)	$\delta(CH_3)$

Table 3.5 Infrared spectrum of Ni : bipy at ratio 1 : 5

Substance	Wavenumber (cm^{-1})	Assignments
Ni : bipy 1 : 5	2900 (vw)	ν_s(CH)
	1860 (vw)	ν(C=N)
	1650 (w)	δ_a(HNH)
	1600 (vw)	C=Cunsymmetrical conjugated diene
	1280 (vw)	ν(C=N)

Table 3.6 Infrared spectrum of Co : NH_3 at various ratio 1 : 3, 1 : 10 and 1 : 25

Substance	Wavenumber (cm^{-1})	Assignments
Co : NH_3 1 : 3	3120 (br)	$\nu_a(NH_3)$
	3000 (w)	$\nu_s(NH_3)$
	1650 (m)	δ_a(HNH)
Co : NH_3 1 : 10	3120 (br)	$\nu_a(NH_3)$
	3000 (w)	$\nu_s(NH_3)$
	1650 (m)	δ_a(HNH)
Co : NH_3 1 : 25	3120 (br)	$\nu_a(NH_3)$
	3000 (w)	$\nu_s(NH_3)$
	1650 (w)	δ_a(HNH)

Table 3.7 Infrared spectrum of Co : en at various ratio 1 : 1 and 1 : 9

Substance	Wavenumber (cm^{-1})	Assignments
Co : en 1 : 1	3210 (w) 3100 (w) 1650 (m)	ν_a(NH) ν_s(NH) δ_a(HNH)
Co :en 1 : 9	3210 (m) 3100 (w) 1650 (m) 1550 (w)	ν_a(NH) ν_s(NH) δ_a(HNH) δ(HNH)

Table 3.8 Infrared spectrum of Co : DMG at ratio 1 : 6

Substance	Wavenumber (cm^{-1})	Assignments
Co : DMG 1 : 6	3050 (vw) 1600 (m) 1420 (m)	ν(OH) δ_s(HNH) $\delta(CH_3)$

Table 3.9 Infrared spectrum of Co : bipy at ratio 1 : 5

Substance	Wavenumber (cm^{-1})	Assignments
Co : bipy 1 : 5	2950 (vw) 1880 (w) 1670 (vw)	ν_s(CH) ν(C=N) δ_a(HNH)

3.1.6 Electronic spectra

Electronic spectra of the solution of Ni-bentonite compound and Co-bentonite compound shown in Fig. 3.9 - 3.22 and solid diffuse reflectance spectra were in Fig. 3.23-3.30.

Table 3.10 Peaks derived of Ni-bentonite treated with model organic ligands in solution

organic ligand added	Absorption peaks of filtrate solution(nm)	Complex	Ref.
NH_3 1 : 3	569(vw),365(sh)	$[Ni(NH_3)]^{2+}$	11
NH_3 1 : 10	572(sh), 362(sh)	$[Ni(NH_3)]^{2+}$	11
NH_3 1 : 25	580(sh)	$[Ni(NH_3)]^{2+}$	11
en 1 : 1	267(sh)	$NiCl_4^{2-}$	12
en 1 : 9	264(m)	$NiCl_4^{2-}$	12
DMG 1 : 6	588(vw), 226(s)	$NiCl_2$	13
bipy 1 : 5	279(s),232(s)	bipy	14

Table 3.11 Peaks derived of Ni-bentonite treated with model organic ligands on clay surface

organic ligand added	Absorption peaks of solid clay(nm)	Complex	Ref.
Syn std.NH_3	700(s), 440(s)	$[Ni(H_2O)_6]^{2+}$	15
NH_3 1 : 3	700(s)	$[Ni(H_2O)_6]^{2+}$	15
NH_3 1 : 10	700(s)	$[Ni(H_2O)_6]^{2+}$	15
NH_3 1 : 25	700(m)	$[Ni(H_2O)_6]^{2+}$	15
Syn std.en	540(s)	$[Nien_3]^{2+}$	16
en 1 : 1	-	-	-
en 1 : 9	-	-	-
Syn std.DMG	540(s)	$[Ni(DMG)_2]^{2+}$	17
DMG 1 : 6	530(s)	$[Ni(DMG)_2]^{2+}$	17
Syn std.bipy	530(s)	$[Ni(bipy)_3]^{2+}$	17
bipy 1 : 5	530(m)	$[Ni(bipy)_3]^{2+}$	17

note: Syn std. mean synthesis standard , prepared by the same method as clay samples but without clay in the system.

Table 3.12 Peaks derived of Co-bentonite treated with model organic ligands in solution

organic ligand added	Absorption peaks of filtrate solution(nm)	Complex	Ref.
NH_3 1 : 3	481(m),356(sh)	$[Co(NH_3)_6]^{3+}$	14
NH_3 1 : 10	476(m),352(sh)	$[Co(NH_3)_6]^{3+}$	14
NH_3 1 : 25	484(m),348(sh)	$[Co(NH_3)_6]^{3+}$	14
en 1 : 1	458(m),339	$[Coen_3]^{2+}$	18,19
en 1 : 9	275(m)	$CoCl_4^{2-}$	20
DMG 1 : 6	581(vw),360(sh), 289(s),251(sh)	$CoCl_2$ $CoCl_4^{2-}$	21, 20
bipy 1 : 5	279(s),232(s)	bipy	14

Table 3.13 Peaks derived of Co-bentonite treated with model organic ligands on clay surface

organic ligand added	Absorption peaks of solid clay(nm)	Complex	Ref.
Syn std.NH_3	700(s), 530(s)	$CoCl_2$, $[Co(NH_3)_6]^{3+}$	21, 17
NH_3 1 : 3	-	-	-
NH_3 1 : 10	-	-	-
NH_3 1 : 25	-	-	-
Syn std.en	700(s), 540(vw)	$CoCl_2$, $[Coen_3]^{2+}$	21, 17
en 1 : 1	700(w), 540(w)	$CoCl_2$, $[Coen_3]^{2+}$	21, 17
en 1 : 9	-	-	-
Syn std.DMG	700(s)	$CoCl_2$	21
DMG 1 : 6	-	-	-
Syn std.bipy	700(s), 540(w)	$CoCl_2$, $[Co(bipy)_3]^{3+}$	21, 22
bipy 1 : 5	540(w)	$[Co(bipy)_3]^{3+}$	21, 22

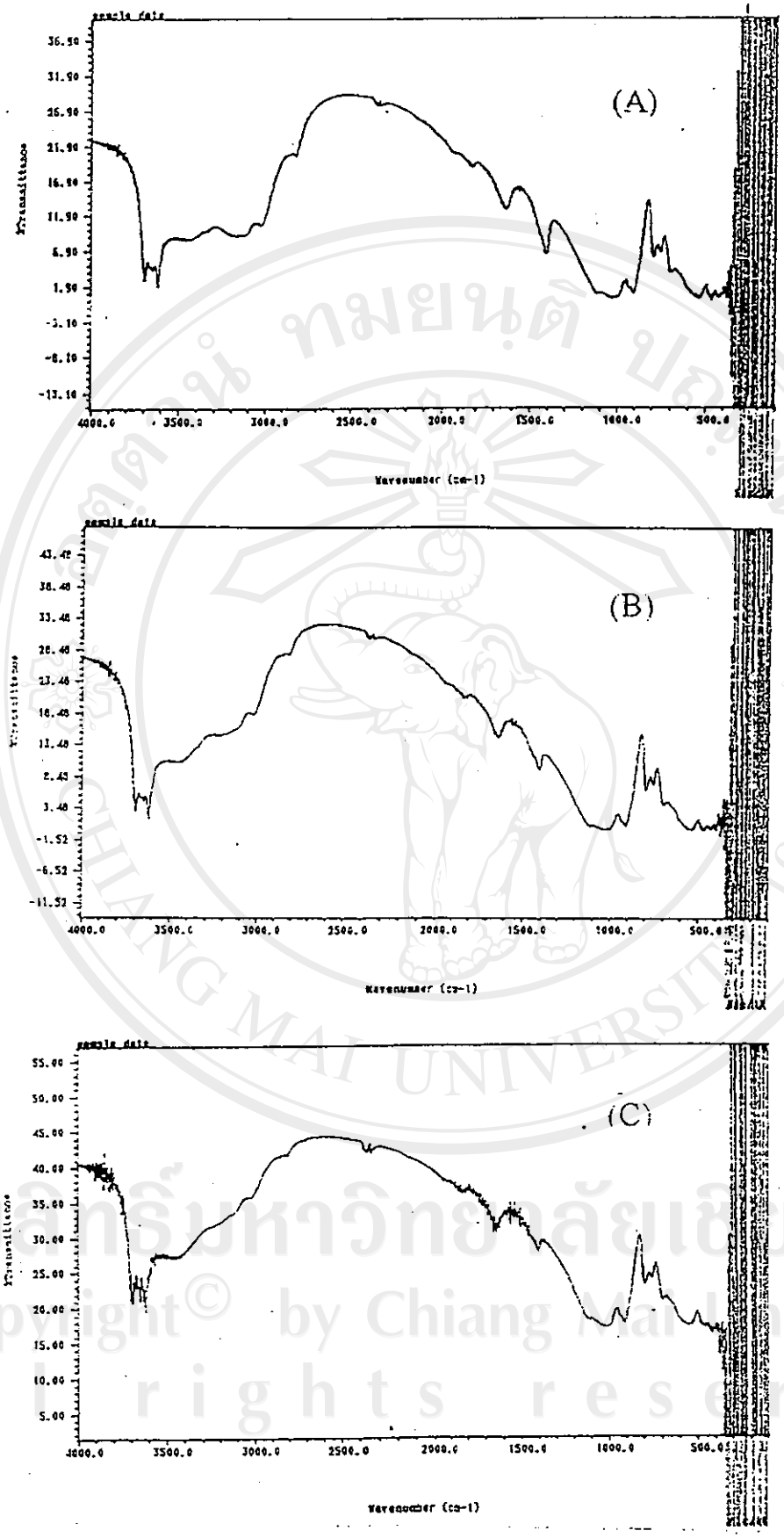

Fig. 3.1 Infrared spectrum of $Ni : NH_3$ at various ratio 1:3 (A), 1 : 10 (B) and 1 : 25 (C)

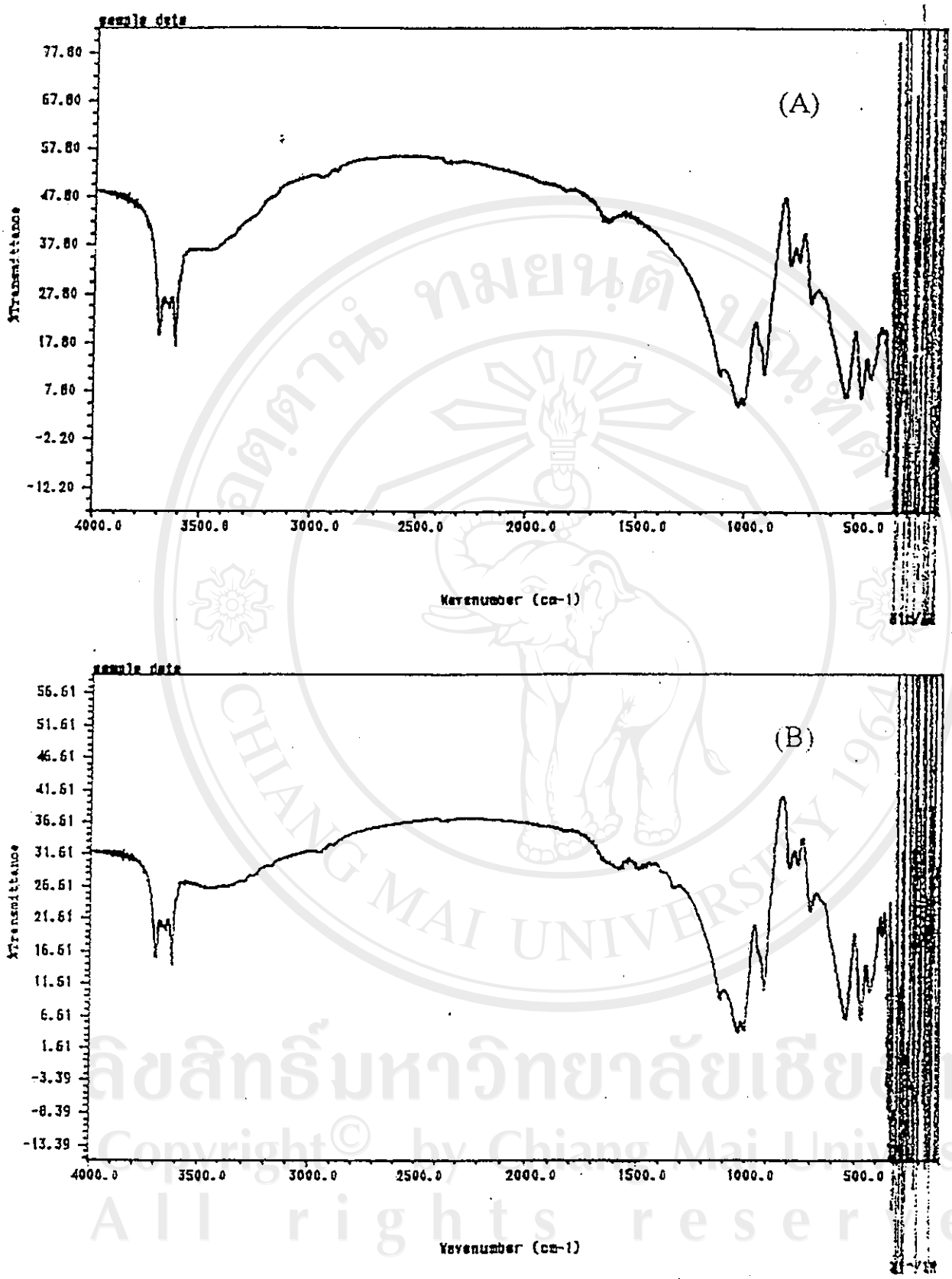

Fig. 3.2 Infrared spectrum of Ni : en at various ratio 1: 1 (A) and 1 : 9 (B)

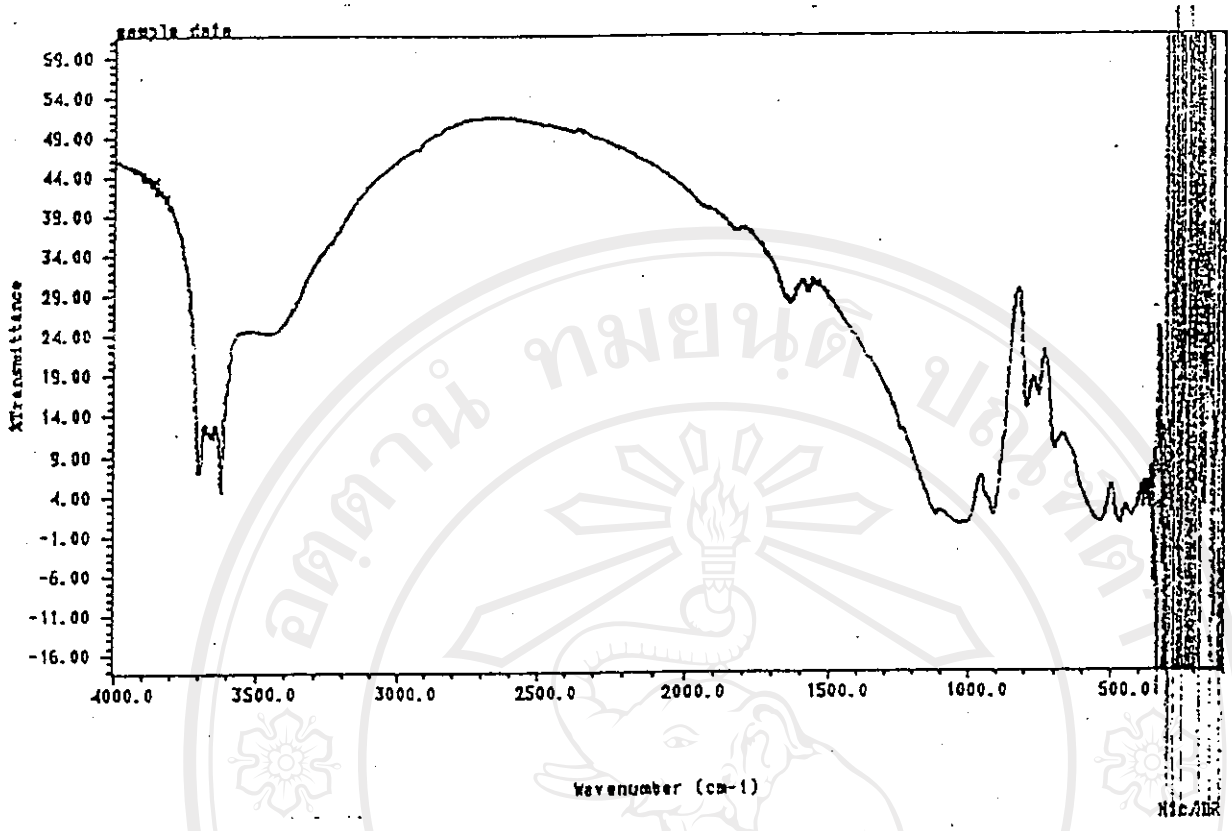

Fig. 3.3 Infrared spectrum of Ni : DMG at ratio 1 : 6

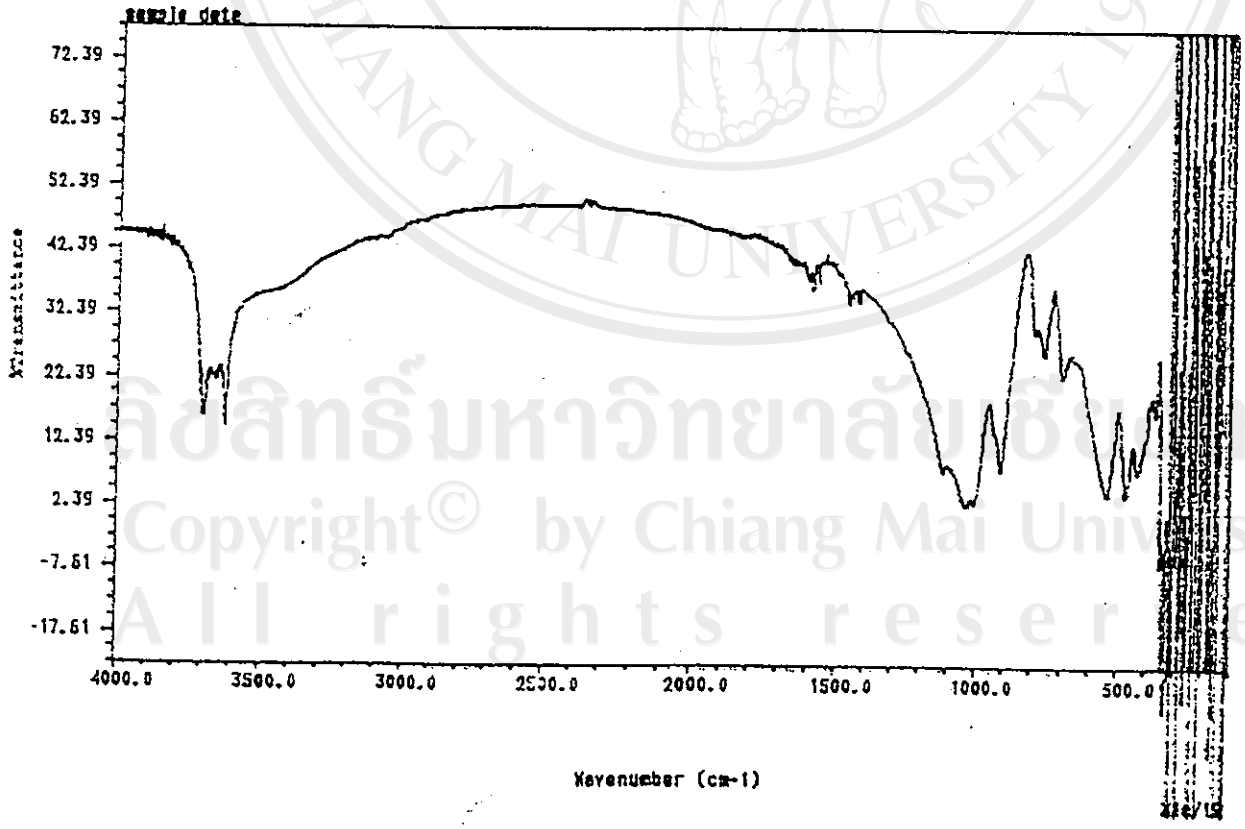

Fig. 3.4 Infrared spectrum of Ni : bipy at ratio 1: 5

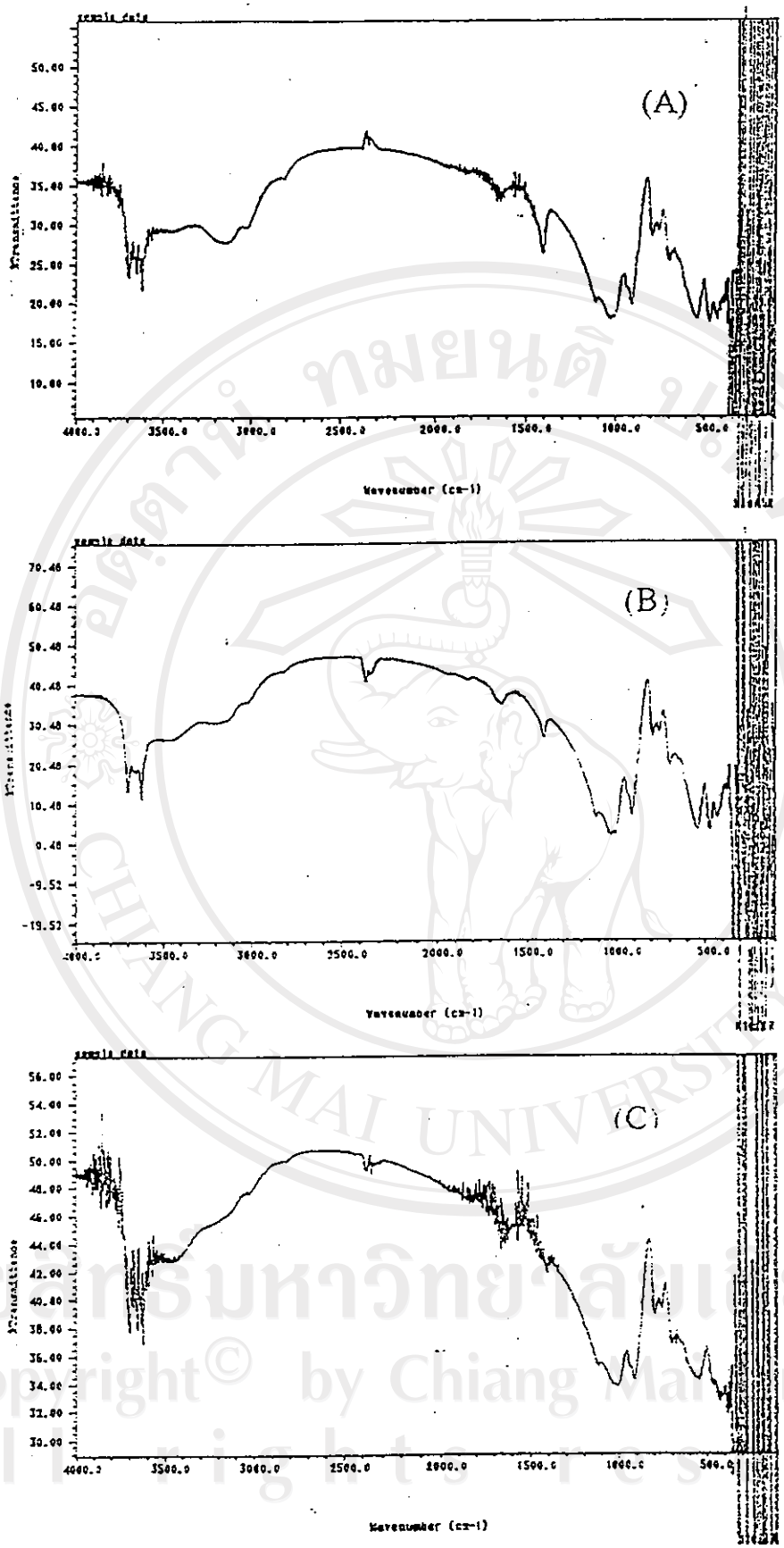

Fig. 3.5 Infrared spectrum of $Co:NH_3$ at various ratio 1:3 (A), 1:10 (B) and 1:25 (C)

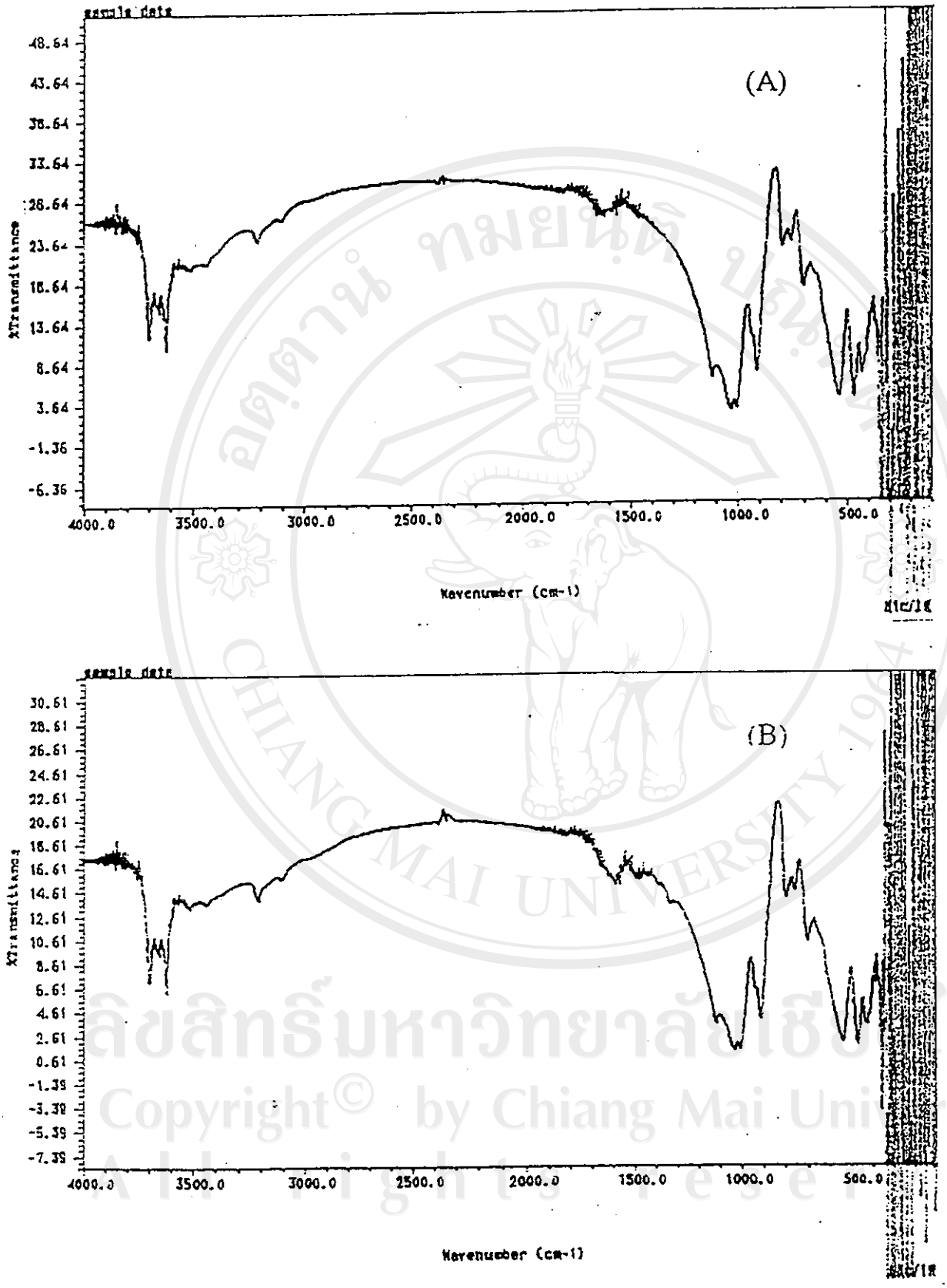

Fig. 3.6 Infrared spectrum of Co : en at various ratio 1: 1 (A) and 1 : 9 (B)

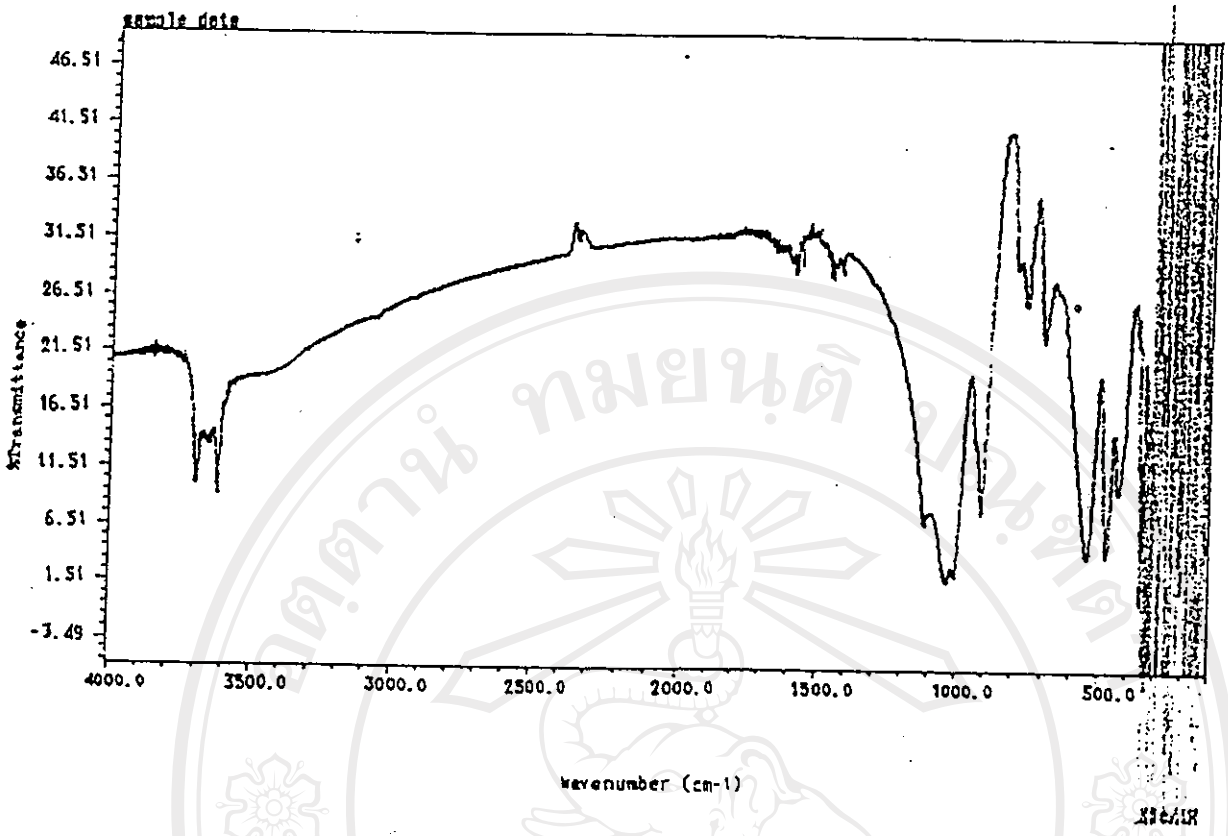

Fig. 3.7 Infrared spectrum of Co : DMG at ratio 1 : 6

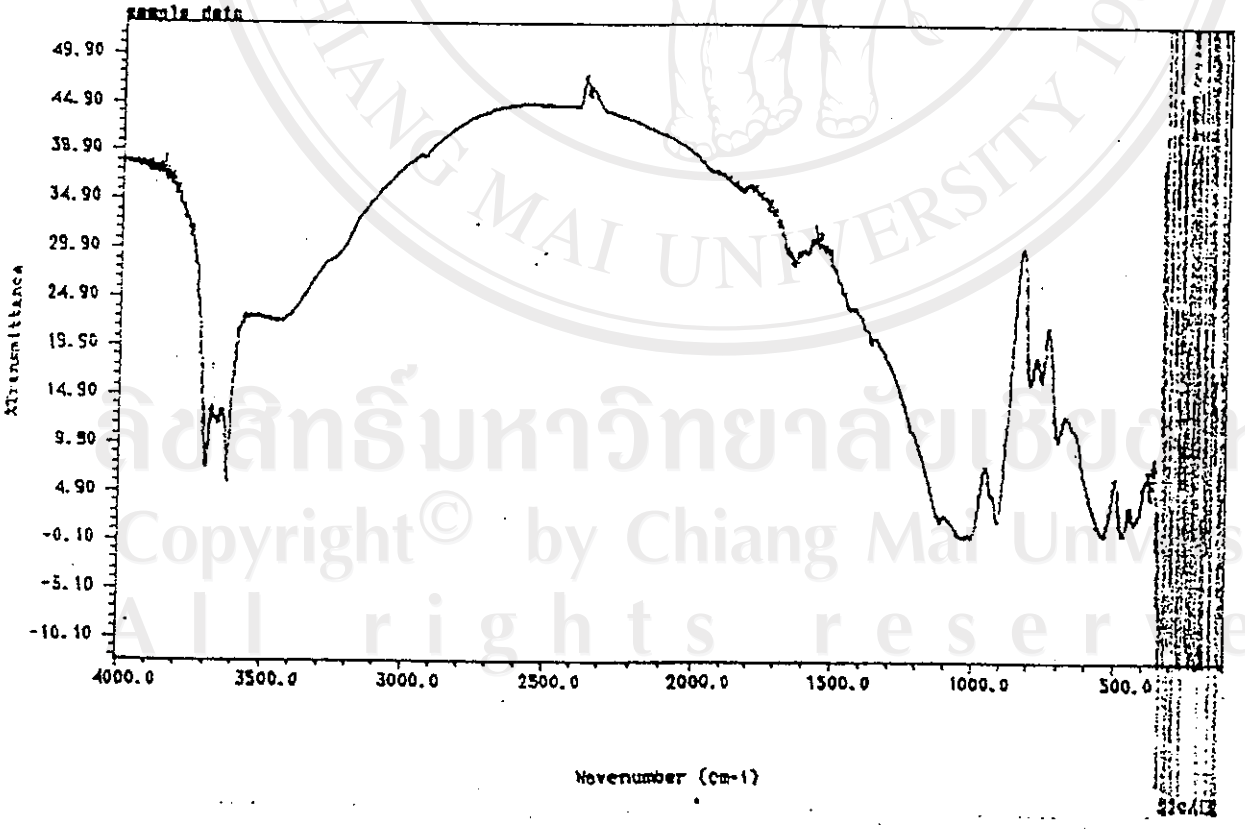

Fig. 3.8 Infrared spectrum of Co : bipy at ratio 1: 5

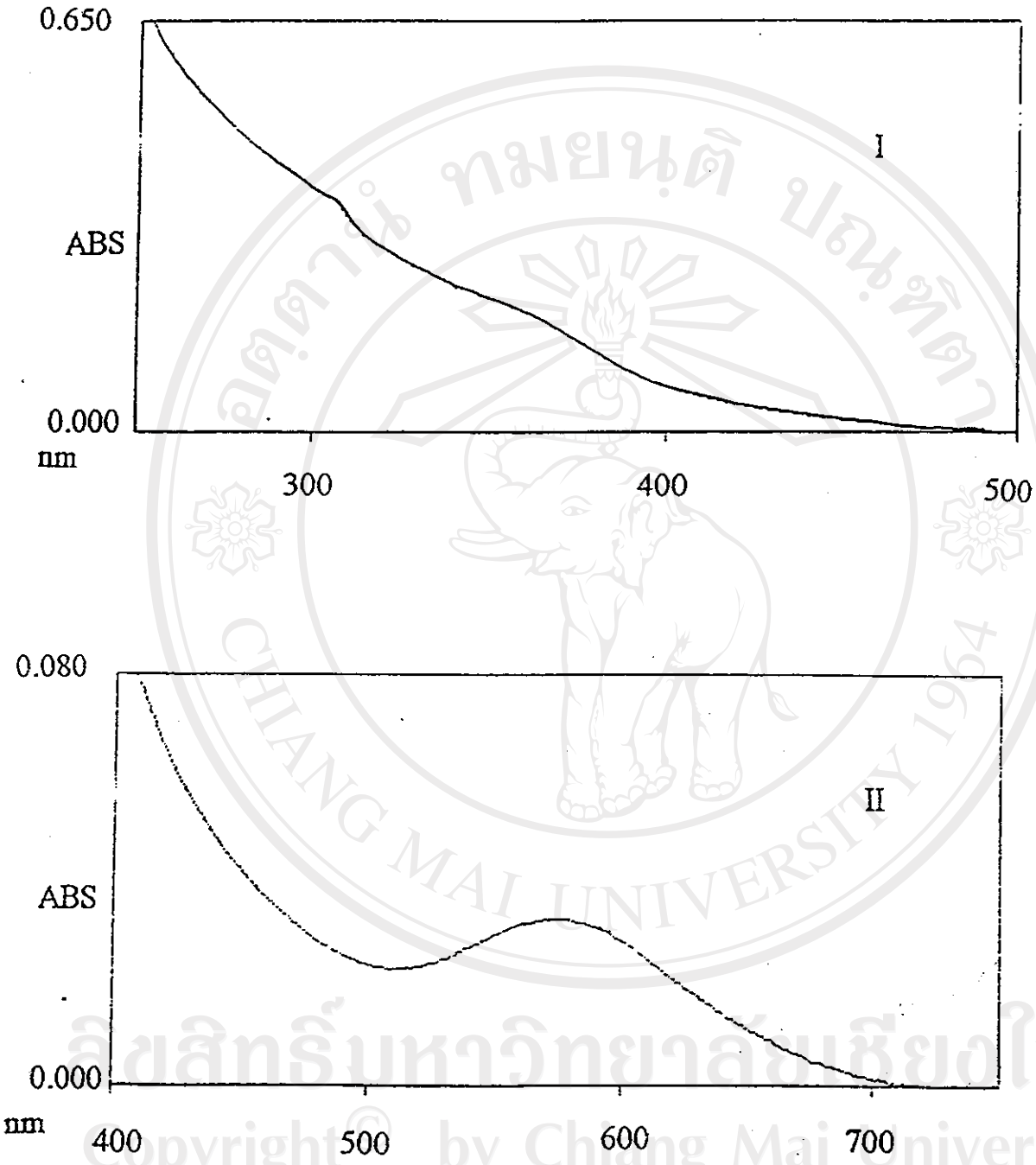

Fig. 3.9 Electronic spectrum of $Ni:NH_3$ at 1 : 3 ratio
I = 280 - 500 nm and II = 400 - 750 nm

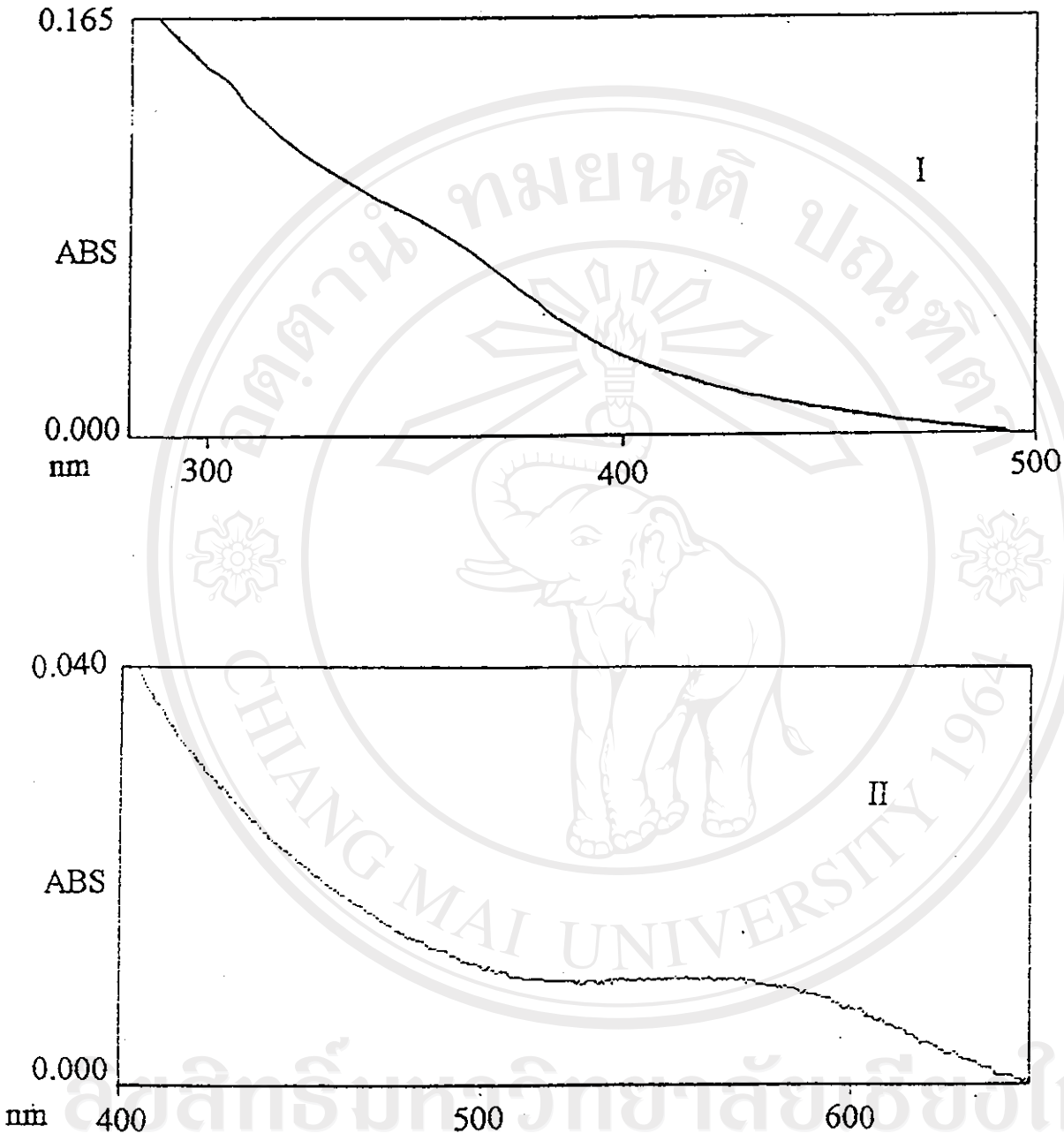

Fig. 3.10 Electronic spectrum of Ni : NH_3 at 1 : 10 ratio
I = 280 - 500 nm and II = 400 - 650 nm

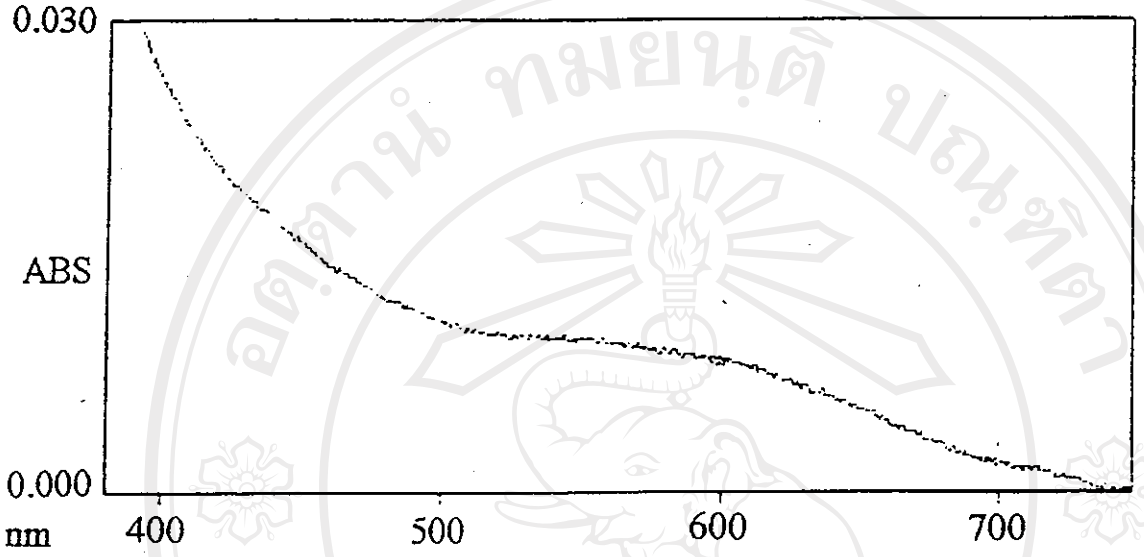

Fig. 3.11 Electronic spectrum of $Ni : NH_3$ at 1 : 25 ratio in range 380 - 750 nm

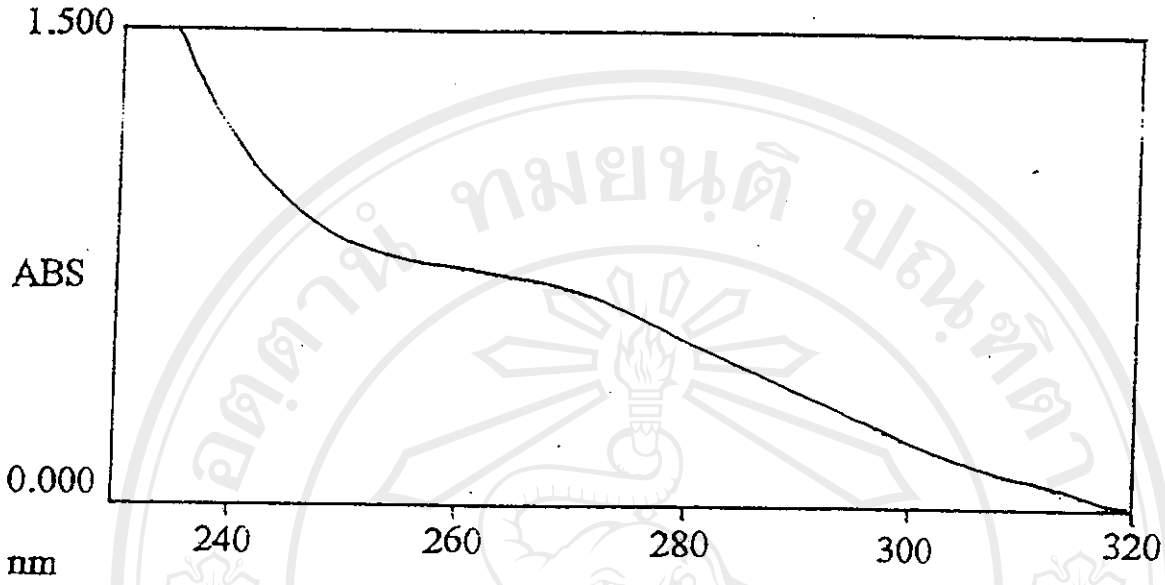

Fig. 3.12 Electronic spectrum of Ni : en at 1 : 1 ratio in range 220 - 320 nm

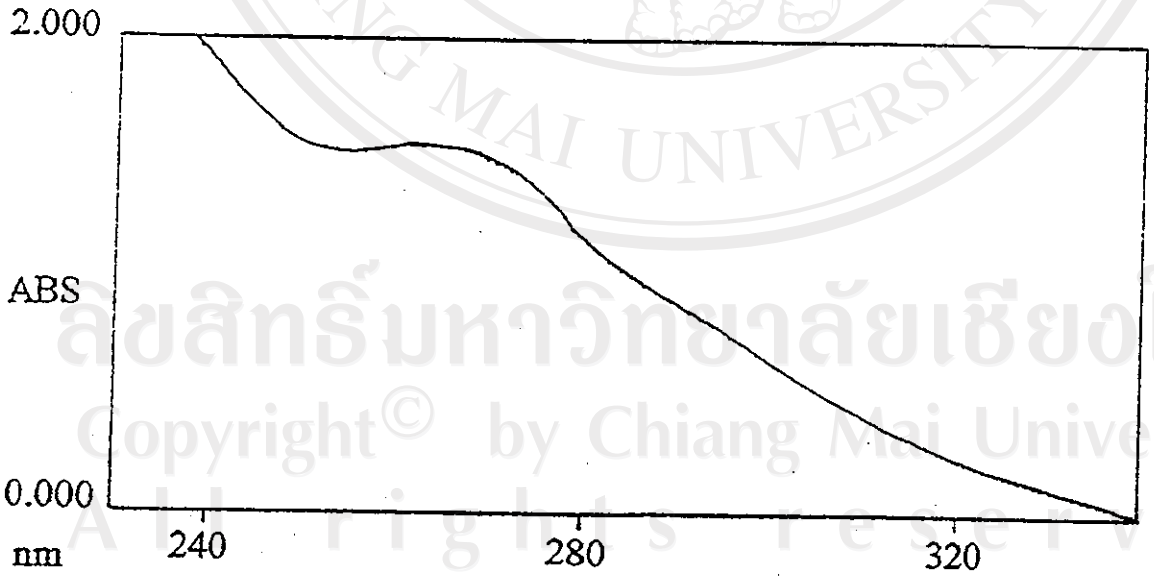

Fig. 3.13 Electronic spectrum of Ni : en at 1 : 9 ratio in range 220 - 350 nm

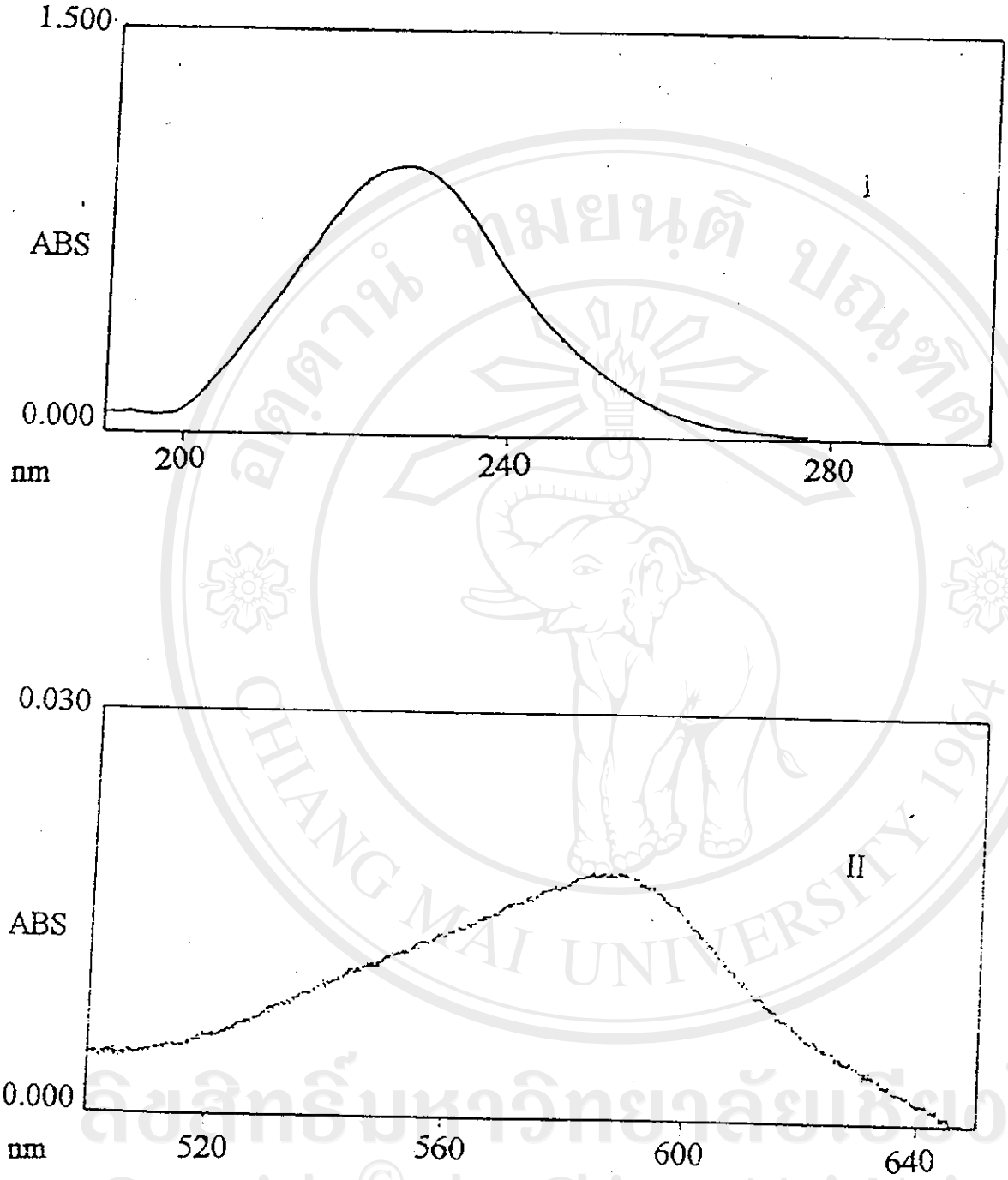

Fig. 3.14 Electronic spectrum of Ni : DMG at 1 : 6 ratio
I = 220 - 300 nm and II = 500 - 660 nm

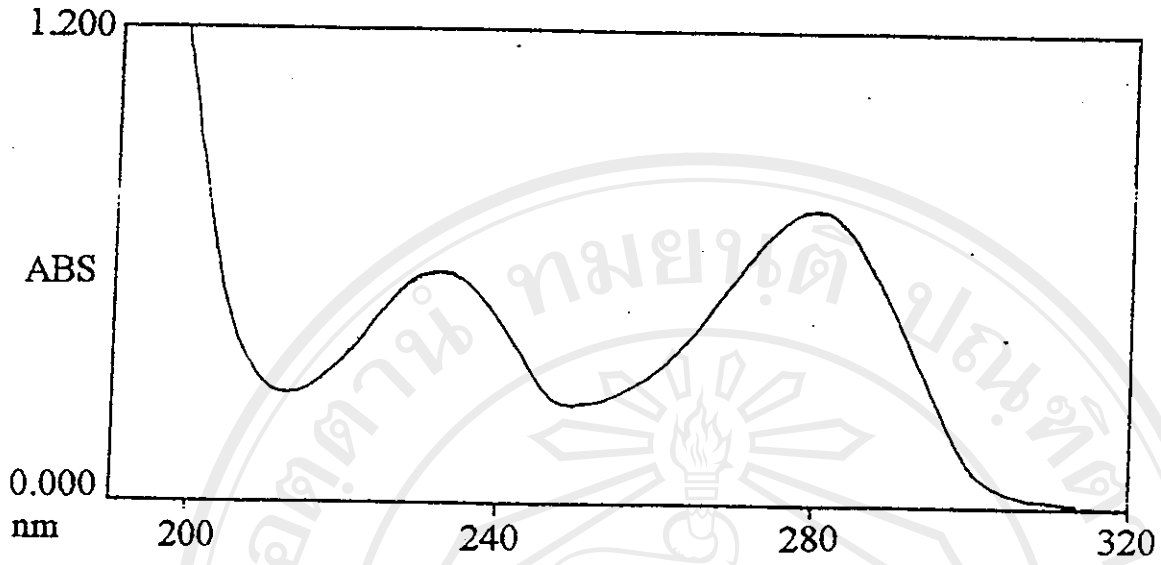

Fig. 3.15 Electronic spectrum of Ni : bipy at 1 : 5 ratio in range 190 - 320 nm

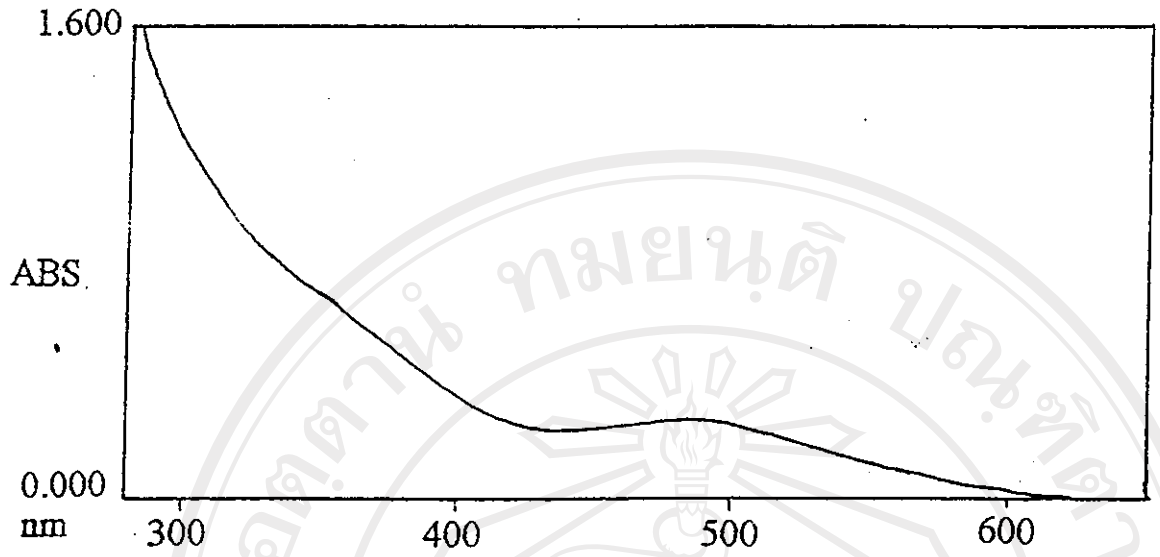

Fig. 3.16 Electronic spectrum of $Co : NH_3$ at 1 : 3 ratio in range 280 - 650 nm

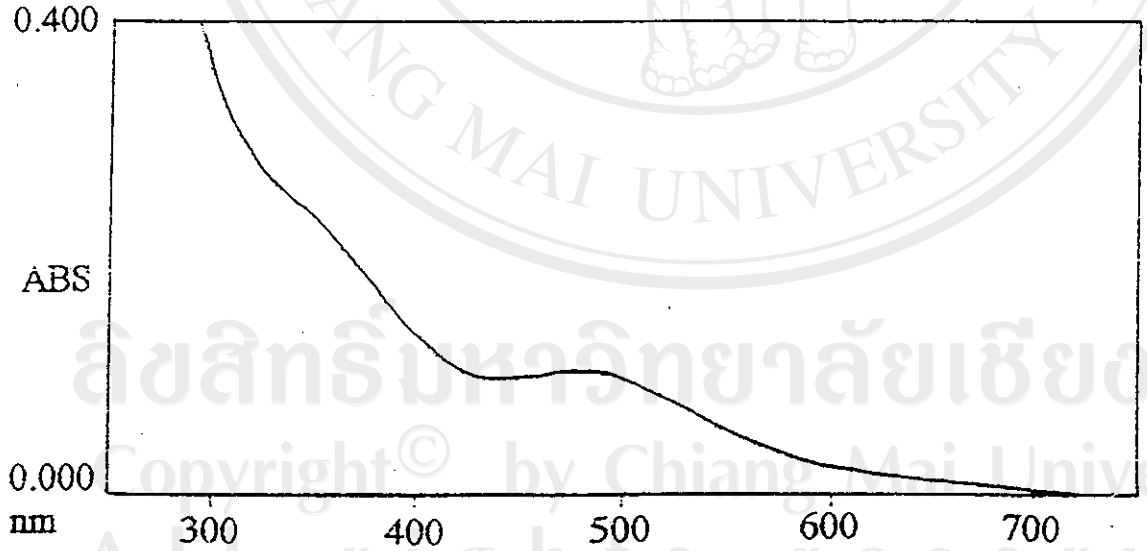

Fig. 3.17 Electronic spectrum of $Co : NH_3$ at 1 : 10 ratio in range 280 - 750 nm

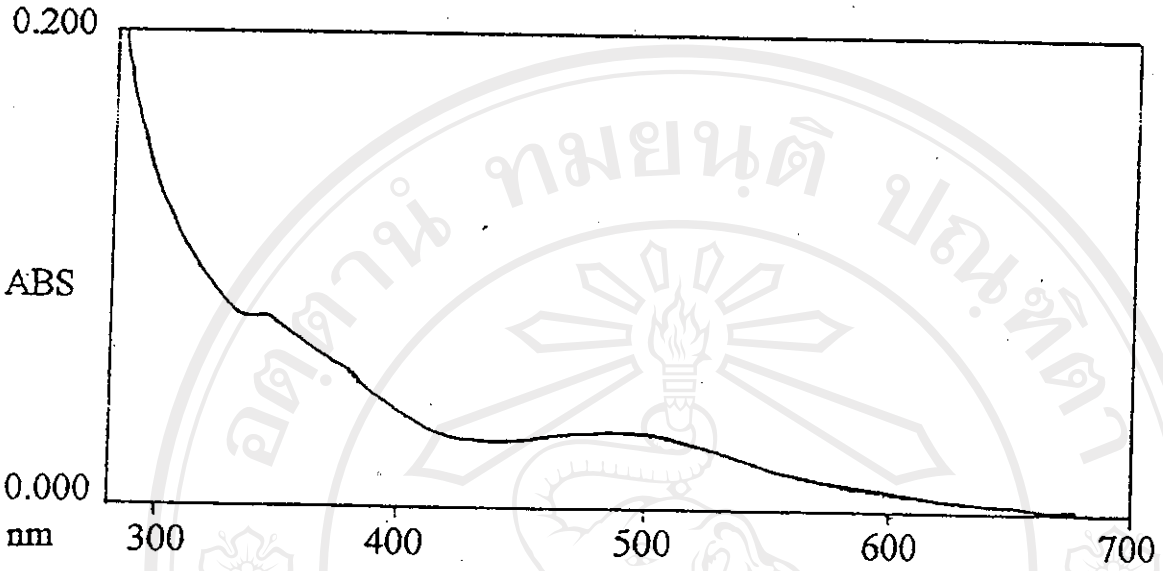

Fig. 3.18 Electronic spectrum of Co : NH_3 at 1 : 25 ratio in range 280 - 700 nm

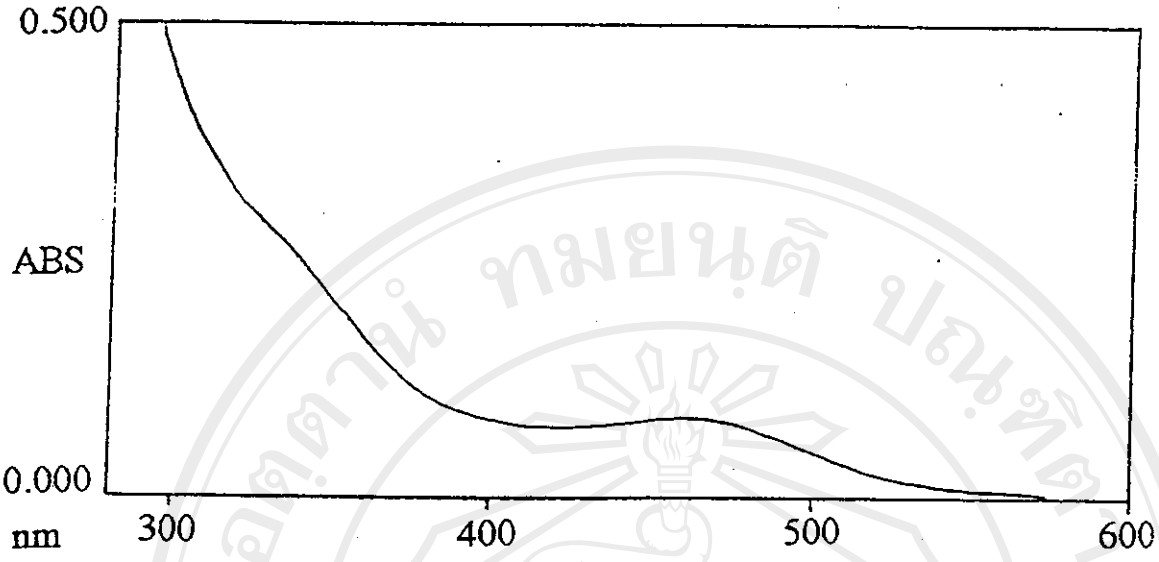

Fig. 3.19 Electronic spectrum of Co : en at 1 : 1 ratio in range 280 - 600 nm

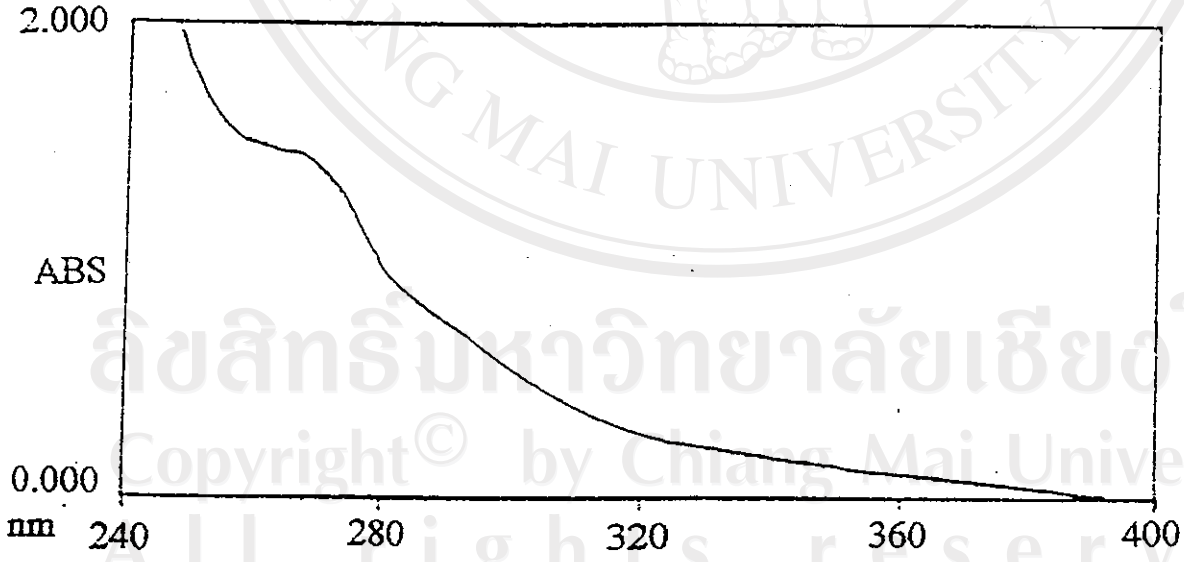

Fig. 3.20 Electronic spectrum of Co : en at 1 : 9 ratio in range 240 - 400 nm

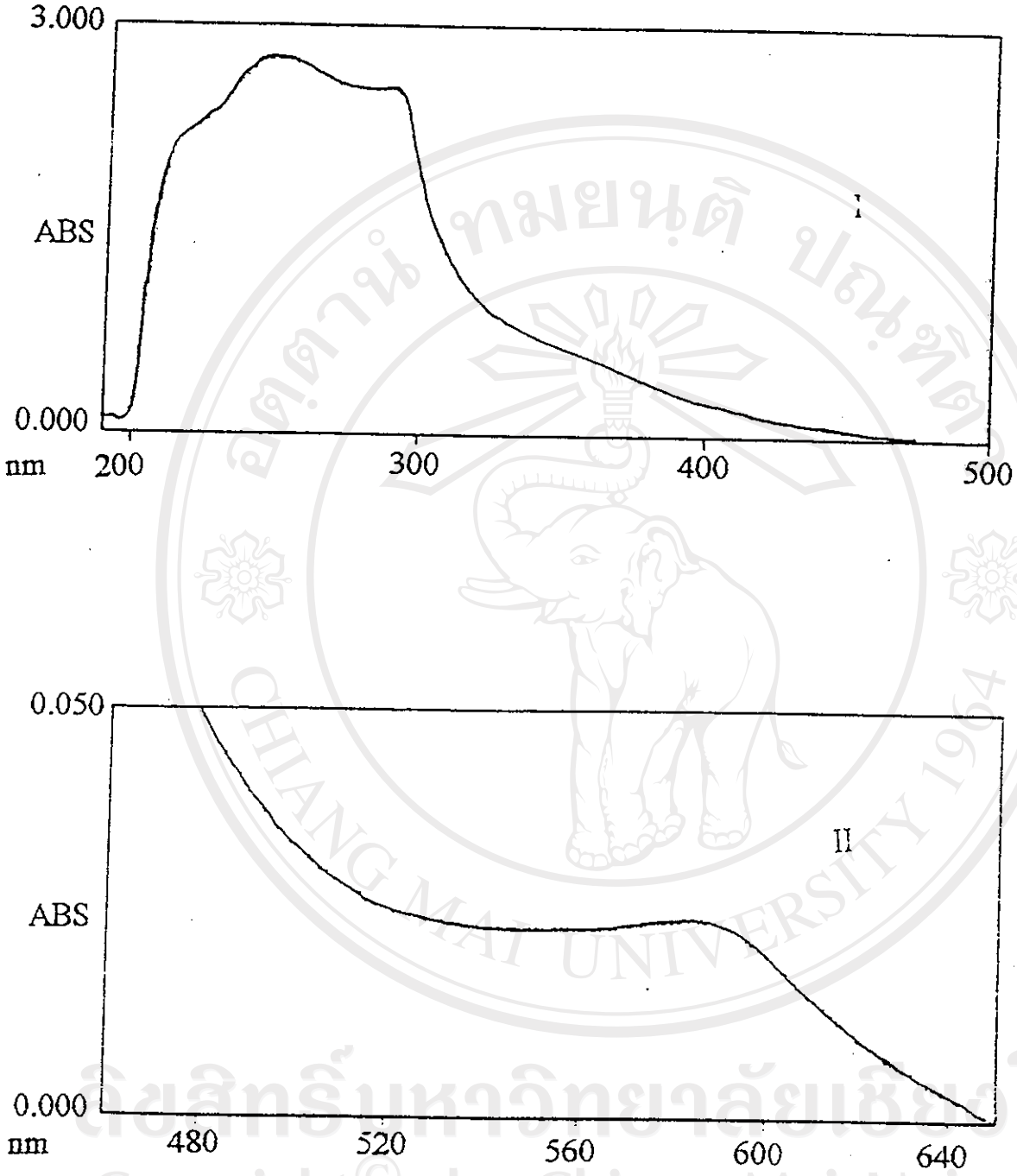

Fig. 3.21 Electronic spectrum of Co : DMG at 1 : 6 ratio
I = 200 - 500 nm and II = 460 - 640 nm

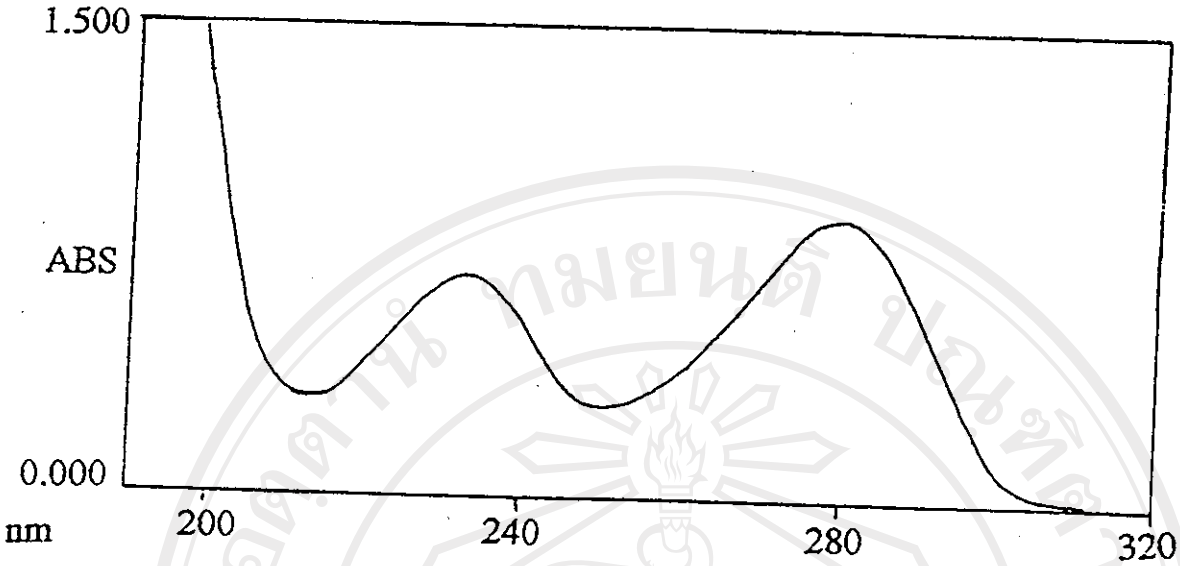

Fig. 3.22 Electronic spectrum of Co : bipy at 1 : 5 ratio in range 190 - 320 nm

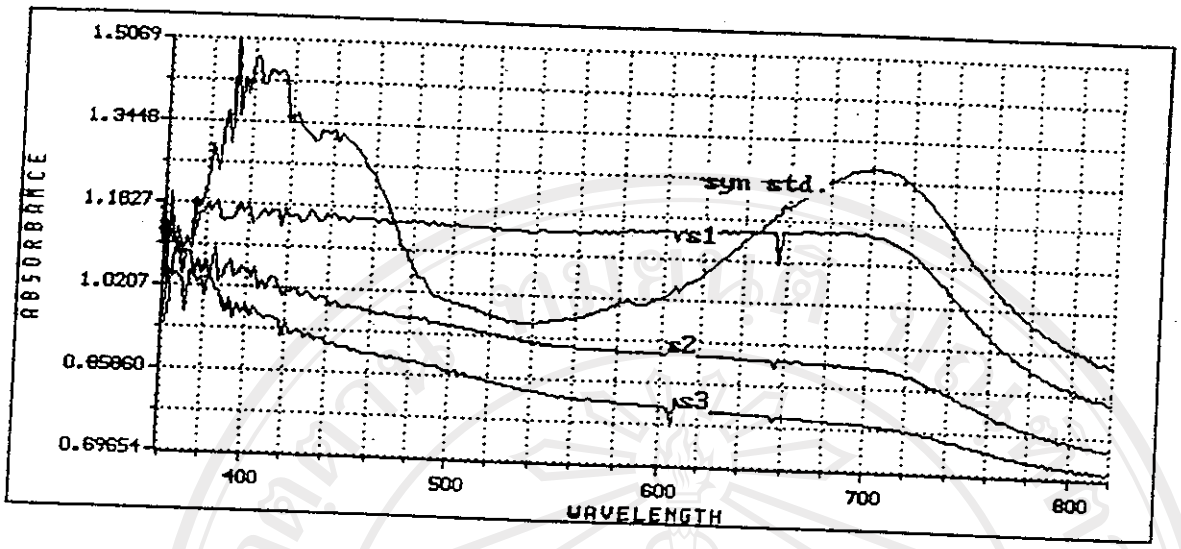

Fig. 3.23 Diffuse reflectance spectrum of Ni : NH_3 at various ratio
syn std.=synthesis standard s1=1:3 s2=1:10 s3=1:25

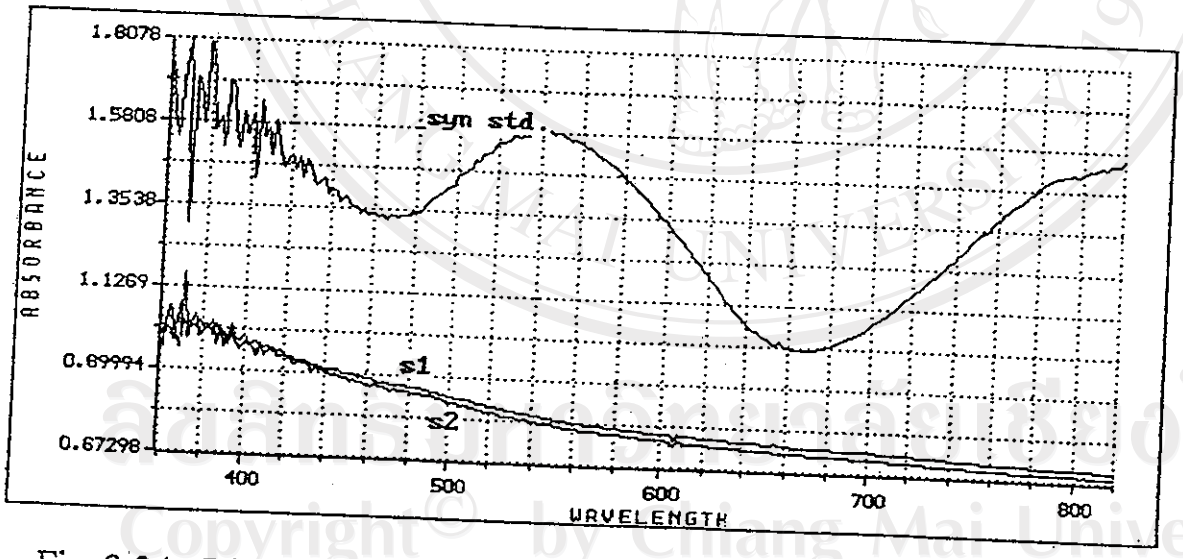

Fig. 3.24 Diffuse reflectance spectrum of Ni : en at various ratio
syn std.=synthesis standard s1=1:1 s2=1:9

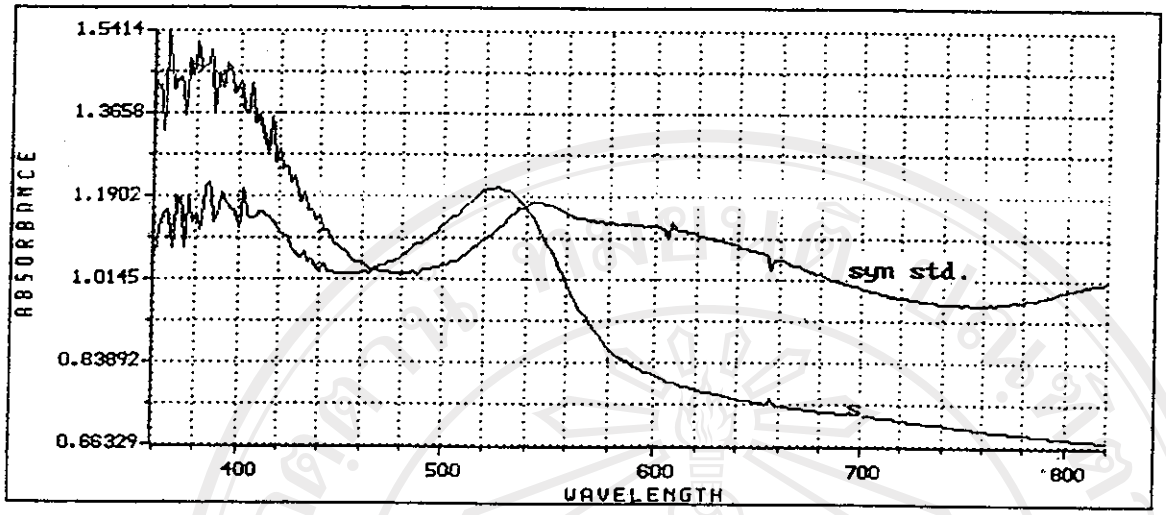

Fig. 3.25 Diffuse reflectance spectrum of Ni : DMG
syn std.=synthesis standard s=1:6

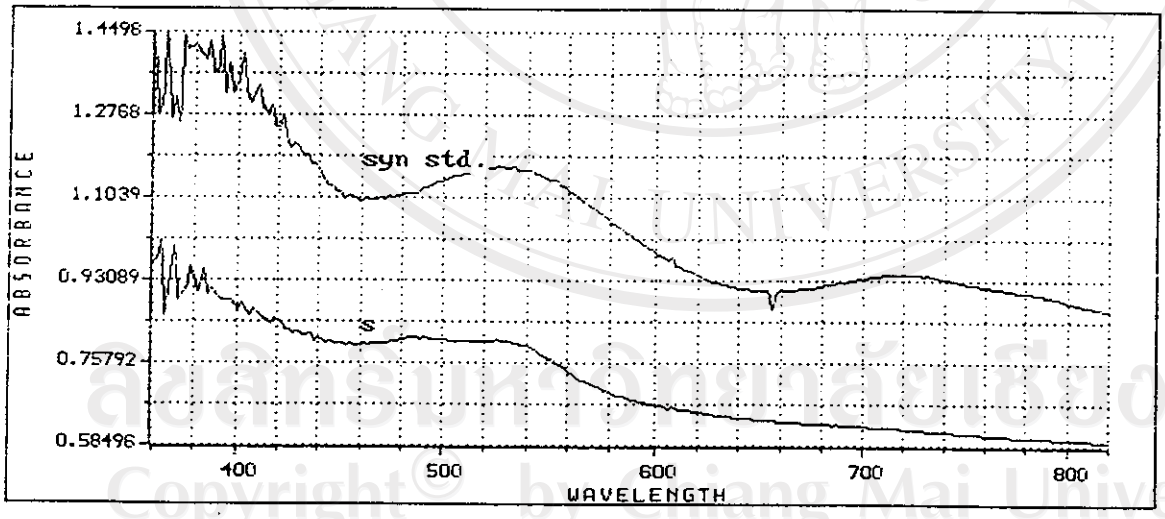

Fig. 3.26 Diffuse reflectance spectrum of Ni : bipy
syn std.=synthesis standard s=1:5

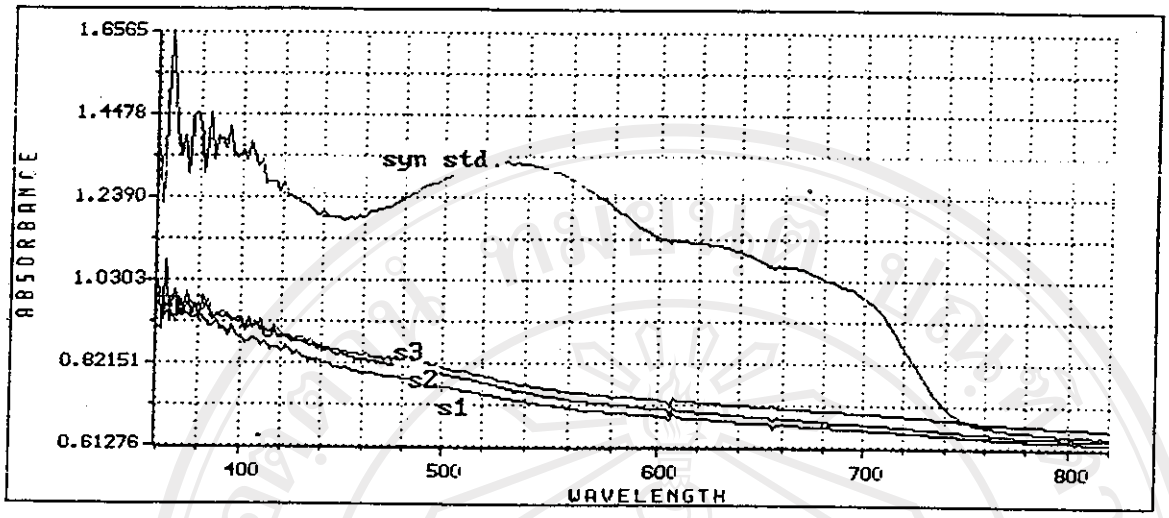

Fig. 3.27 Diffuse reflectance spectrum of Co : NH_3 at various ratio syn std.=synthesis standard s1=1:3 s2=1:10 s3=1:25

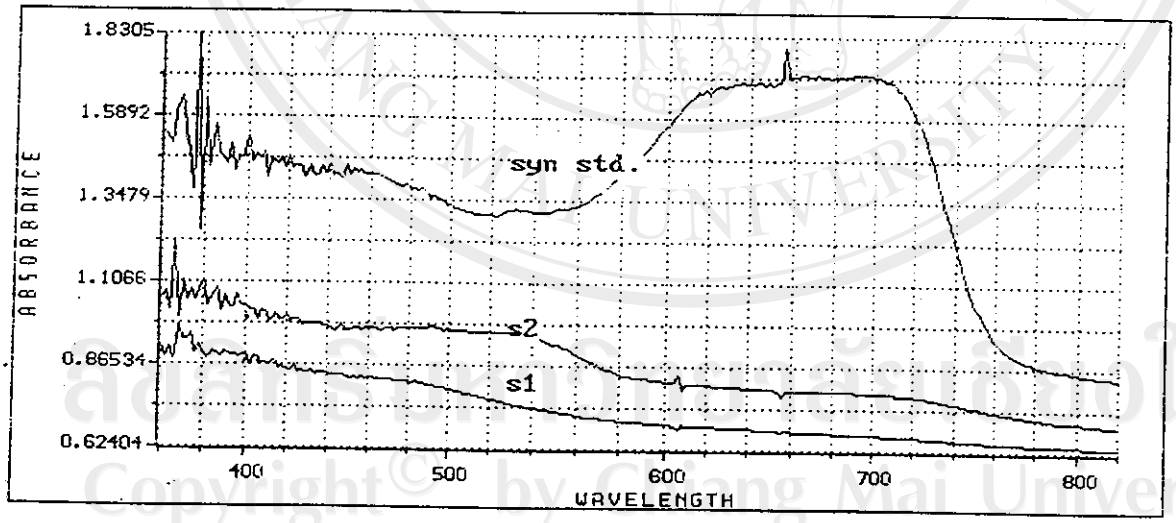

Fig. 3.28 Diffuse reflectance spectrum of Co : en at various ratio syn std.=synthesis standard s1=1:1 s2=1:9

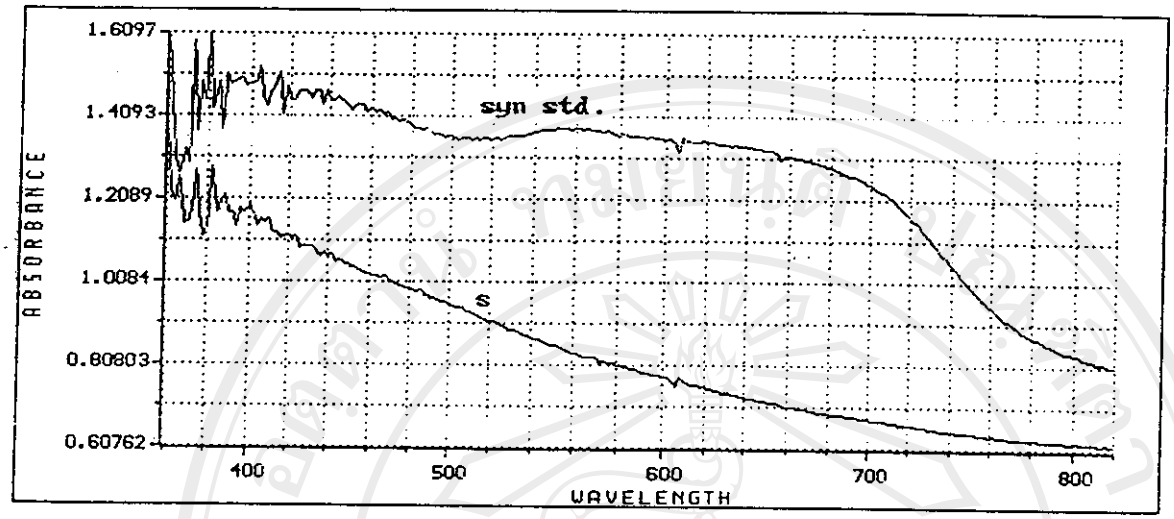

Fig. 3.29 Diffuse reflectance spectrum of Co : DMG
syn std.=synthesis standard s=1:6

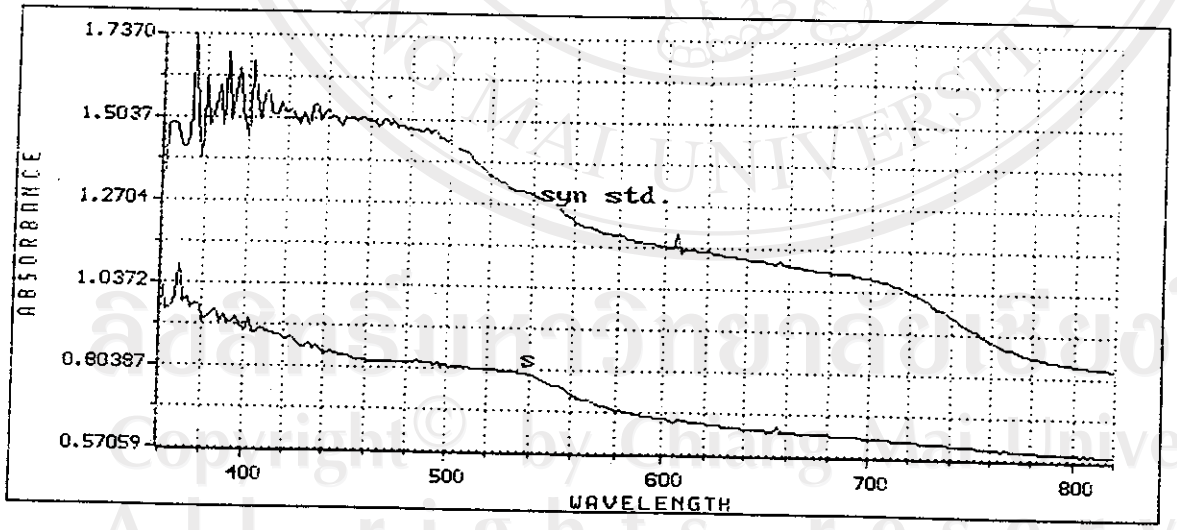

Fig. 3.30 Diffuse reflectance spectrum of Co : bipy
syn std.=synthesis standard s=1:5

3.2 Typical grounwater ligands with nickel and cobalt bentonite

3.2.1 Preparation of samples of Ni-bentonite/1M and Co-bentonite/1M

A more quantitative approach was adopted for this section of the investigation, thus initially the following procedure was used to prepare clay samples.

Procedure

A sample of bentonite (15 g) was shaken with 0.1 M nickel chloride (or cobalt chloride) solution (150 ml) for 3 days, filtered, then redispersed in a 1 M solution of $NiCl_2$ (or $CoCl_2$) (150 ml) and shaken for a future 3 days prior to filteration. The clay was dispersed in deionized water (100 ml), shaken for 2 h, then separated by filteration.

Portion of the clay 1 g was digested by nitric aqua regia digestion. Quantitative analysis of nickel and cobalt in Ni-bentonite/1M and Co-bentonite/1M was carried out by using Atomic absorption spectrophotometry.

3.2.2 Result of Atomic absorption spectrophotometry

Clay, untreated with $NiCl_2$ and $CoCl_2$ solution contained
nickel 3.49×10^{-3} mmole/g and
cobalt 5.53×10^{-3} mmole/g.

Nickel-bentonite clay sample contained
nickel 5.64 mmole/g.

Cobalt-bentonite clay sample contained
cobalt 4.58 mmole/g.

3.2.3 Reaction with ligands

3.2.3.1 Reaction with equal ligand concentration

Portion of the four clay types (0.2 g) were covered separately with solutions (10 ml) of ammonia (1.2 M), en (1.2 M), butanoic acid (Ba, 1.2 M) and with deionized water. The mixtures were stirred for 3 days and then filtered. The solids were air-dried at room temperature, each clay specimen was examined by IR and Diffuse reflectance analysis. Liquids were retained for analysis. The appropriate ligand/metal reaction ratios were:

Ni-bentonite/1M = 10.6 : 1
Co-bentonite/1M = 13.1 : 1

Colour of Ni-bentonite/1M and Co-bentonite/1M showed in Table 3.12. Results of Ni released, Co released and pH showed in Table 3.13 and 3.14, respectively.

Table 3.14 Colour of Ni-bentonite/1M and Co-bentonite/1M clays samples after treatment with solutions of organic ligands

organic added	Colour of solid product	
	Ni-bentonite/1M	Co-bentonite/1M
NH_3	green	pink
en	brown	orange
BA	-	-
Blank-dw	-	-

Table 3.15 Physical characteristics of solution remaining from treatment of Ni-bentonite clays with organic ligands

organic added	colour of solution	Initial solution pH	Final solution pH	Ni released from clay mmole/1g	Percent Ni released
NH_3	-	10.88	10.50	1.25	33.33
en	brown	10.78	11.17	1.60	42.67
BA	-	2.66	2.54	3.25	86.67
blank-dw	-	5.87	5.49	1.25	33.33

dw = deionized water

Table 3.16 Physical characteristics of solution remaining from treatment of Co-bentonite clays with organic ligands

organic added	colour of solution	Initial solution pH	Final solution pH	Ni released from clay mmole/1g	Percent Ni released
NH_3	pink	10.78	10.71	1.05	35.00
en	orange	10.93	11.22	1.15	38.33
BA	-	2.63	2.80	2.75	91.67
blank-dw	-	5.9	6.65	1.10	36.67

3.2.3.2 Infrared spectra

The solid of each nickel compounds and cobalt compounds on clay sample was scannined in the infrared region and its spectrum was recorded by KBr disc method.

The following absorption bands are characteristices of Ni-bentonite compounds. They were tabulated in Table 3.17-3.18 and shown in Fig. 3.31-3.38.

Table 3.17 Physical characteristics of Ni-bentonite/1M after treatement with solution of organic ligands

Substance	Wavenumber (cm^{-1})	Assignments
NH_3	3100 (w) 3000 (vw) 1400 (m)	$\nu_a(NH_3)$ $\nu_s(NH_3)$ $\delta_a(HNH)$
en	3250 (vw) 3150 (vw) 2950 (w) 2870 (w) 1490 (vw)	$\nu_a(NH)$ $\nu_s(NH)$ $\nu_s(CH_2)$ $\delta(HNH)$
BA	2930 (vw) 2850 (vw)	$\nu_s(CH_2)$
Blank-dw	2830 (vw)	$\nu_s(CH_2)$

Table 3.18 Physical characteristics of Co-bentonite/1M after treatement with solution of organic ligands

Substance	Wavenumber (cm^{-1})	Assignments
NH_3	3150 (w) 1400 (m)	$\nu_a(NH_3)$ $\delta_a(HNH)$
en	3200 (m) 3100 (w) 2950 (vw) 1550 (vw)	$\nu_a(NH)$ $\nu_s(NH)$ $\nu_s(CH_2)$ $\delta(HNH)$
BA	-	-
Blank-dw	-	-

3.2.3.3 Electronic spectra

Ni-bentonite/1M and Co-bentonite/1M were contacted with three ligands and water. Same concentration and equal volume of ligands were used in this step, the spectra were tabulated in Table 3.19-3.22 and shown in Fig. 3.39-3.46.

Table 3.19 Peaks derived from electronic spectrum of Ni-bentonite/1M treated with organic ligand solutions at equal concentration in solution

Organic added	Absorption peaks of filtrate solution(nm)	Complex	Ref.
NH_3	341(sh),304(m), 294(m)	$[Ni(H_2O)_6]^{2+}$, $NiCl_4^{2-}$	15, 12
en	341(sh)	$Nien_3^{2+}$	16
BA	381(sh),305(m), 297(m)	$[Ni(H_2O)_6]^{2+}$, $NiCl_4^{2-}$	15, 12
Blank-dw	305(w),297(sh)	$NiCl_4^{2-}$	12

Table 3.20 Peaks derived from electronic spectrum of Ni-bentonite/1M treated with organic ligand solutions at equal concentration on clay surface

Organic added	Absorption peaks of solid clay(nm)	Complex	Ref
NH_3	530(m)	$[Ni(NH_3)_6]^{2+}$	17
en	700(s)	$[Ni(H_2O)_6]^{2+}$	15
BA	-	-	-
Blank-dw	700(w)	$[Ni(H_2O)_6]^{2+}$	15

Table 3.21 Peaks derived from electronic spectrum of Co-bentonite/1M treated with organic ligand solutions at equal concentration in solution

Organic added	Absorption peaks(nm)	Complex	Ref.
NH_3	491(w), 350(sh)	$[Co(NH_3)_6]^{3+}$	14
en	467(w), 350(sh)	$Coen_3^{3+}$	18,19
BA	305(w)	-	-
Blank-dw	248(w), 207(sh)	$CoCl_4^{2-}$	20

Table 3.22 Peaks derived from electronic spectrum of Co-bentonite/1M treated with organic ligand solutions at equal concentration in solution

Organic added	Absorption peaks of solid clay(nm)	Complex	Ref.
NH_3	500(m)	$[Co(NH_3)_6]^{3+}$	17
en	530(m)	$Coen_3^{3+}$	17
BA	700(m)	$CoCl_2$	21
Blank-dw	-	-	-

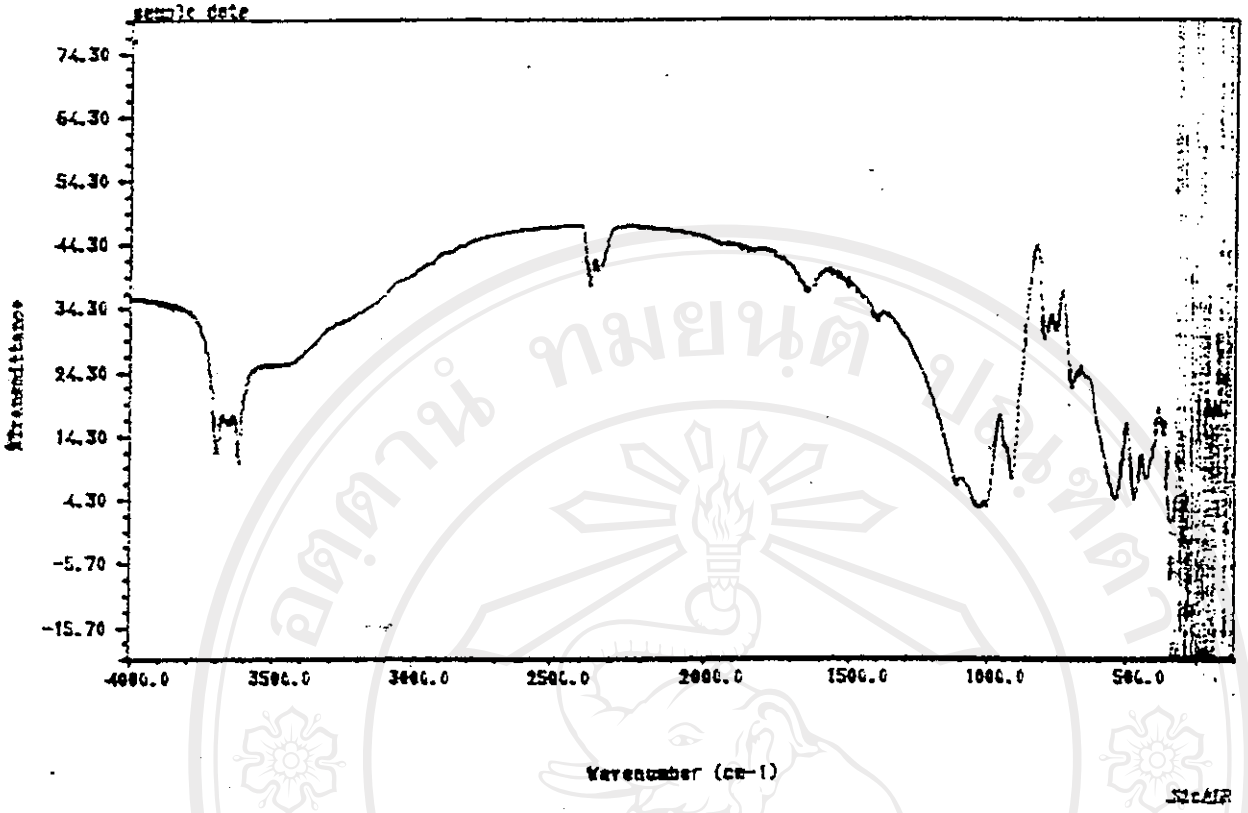

Fig. 3.31 Infrared spectrum of Ni : NH_3 at ratio 10.6 : 1

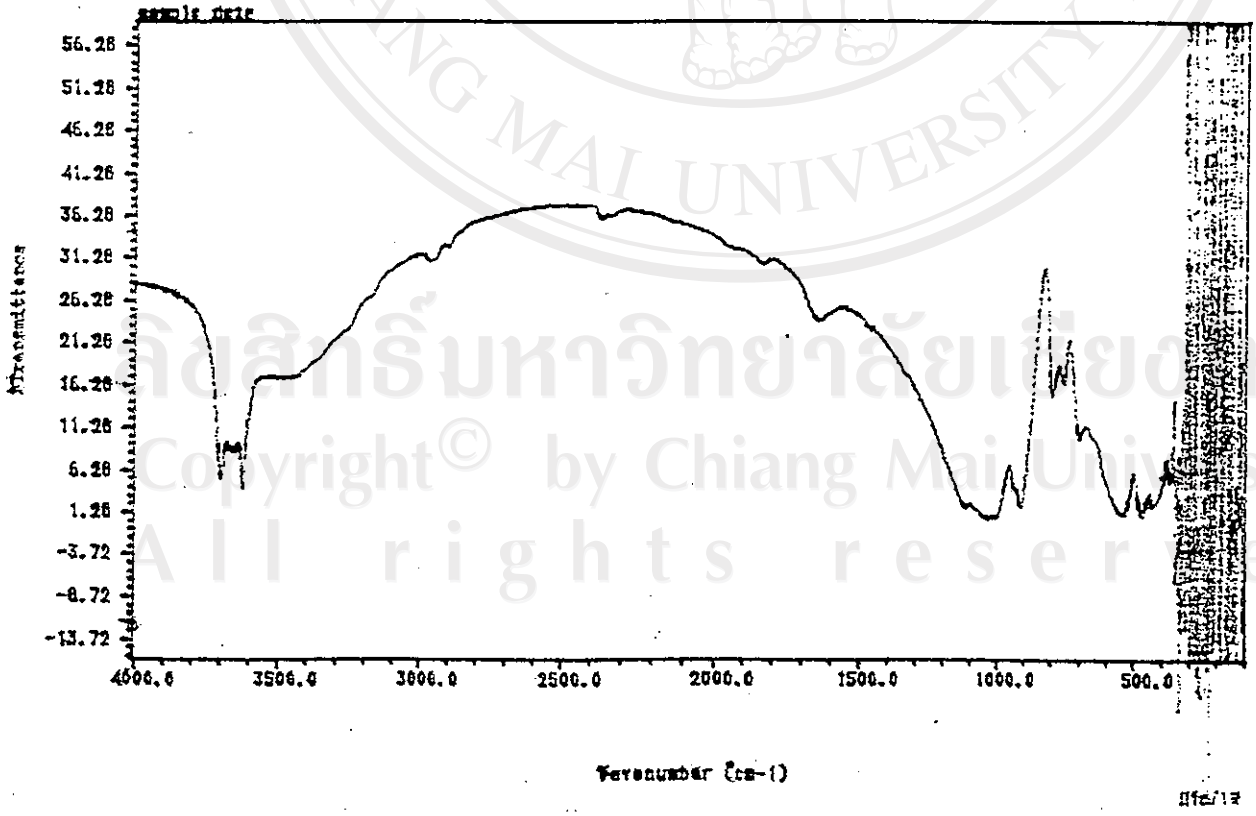

Fig. 3.32 Infrared spectrum of Ni : en at ratio 10.6 : 1

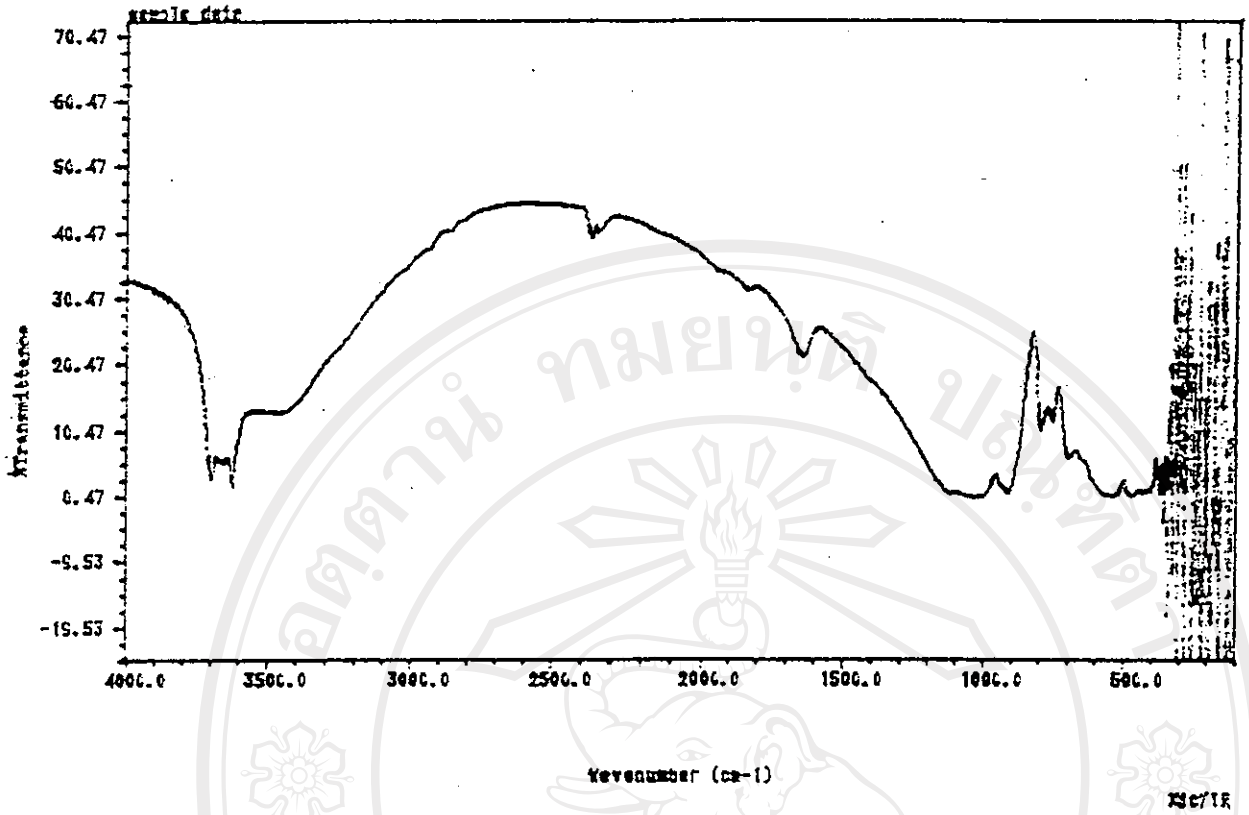

Fig. 3.33 Infrared spectrum of Ni : BA at ratio 10.6 : 1

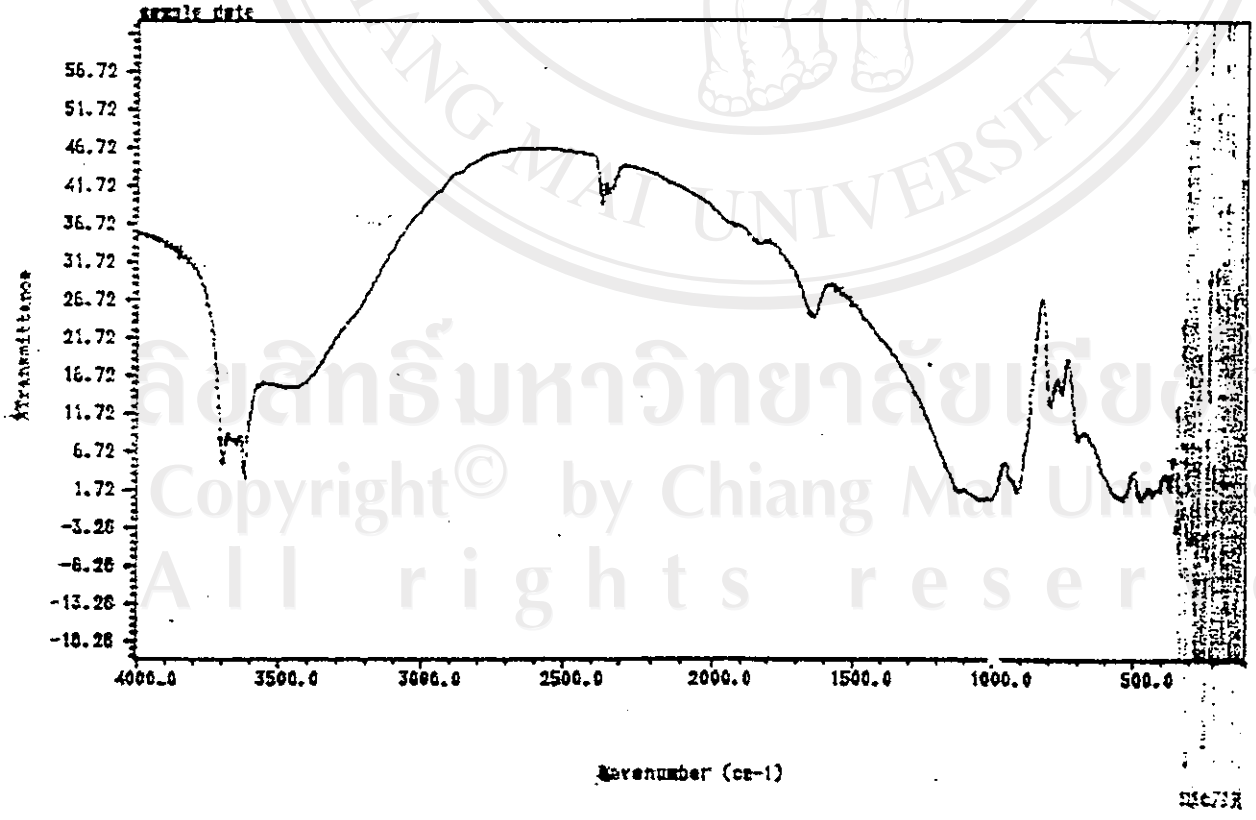

Fig. 3.34 Infrared spectrum of Ni-bentonite with deionize water

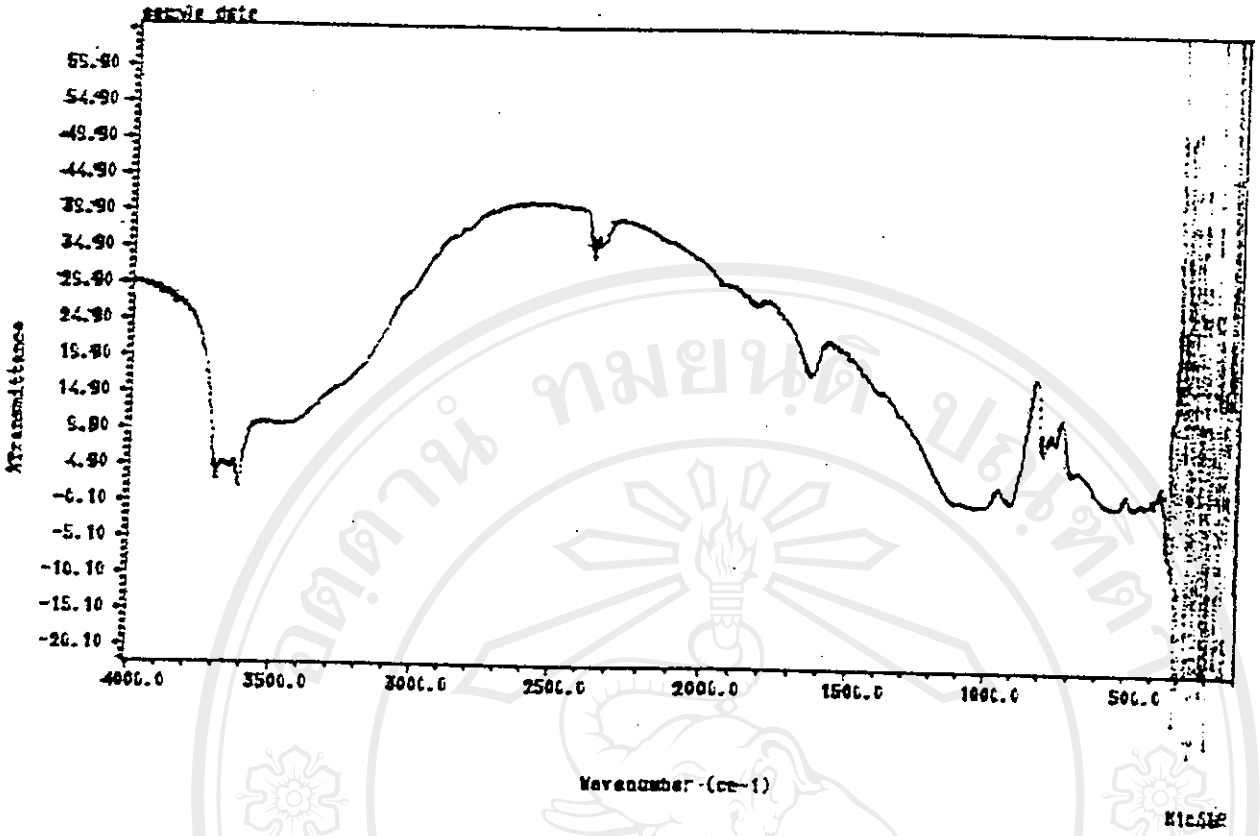

Fig. 3.35 Infrared spectrum of Co : NH_3 at ratio 13.1 : 1

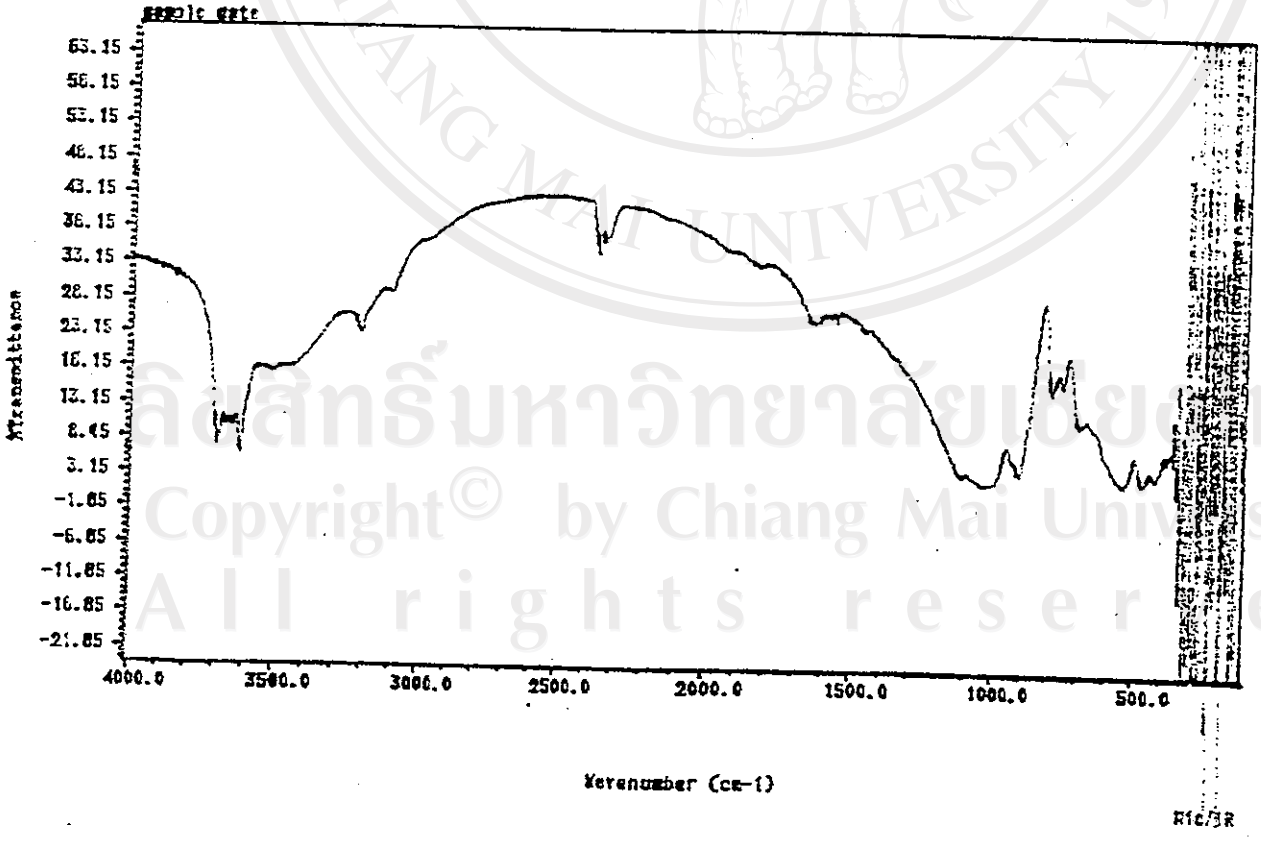

Fig. 3.36 Infrared spectrum of Co : en at ratio 13.1 : 1

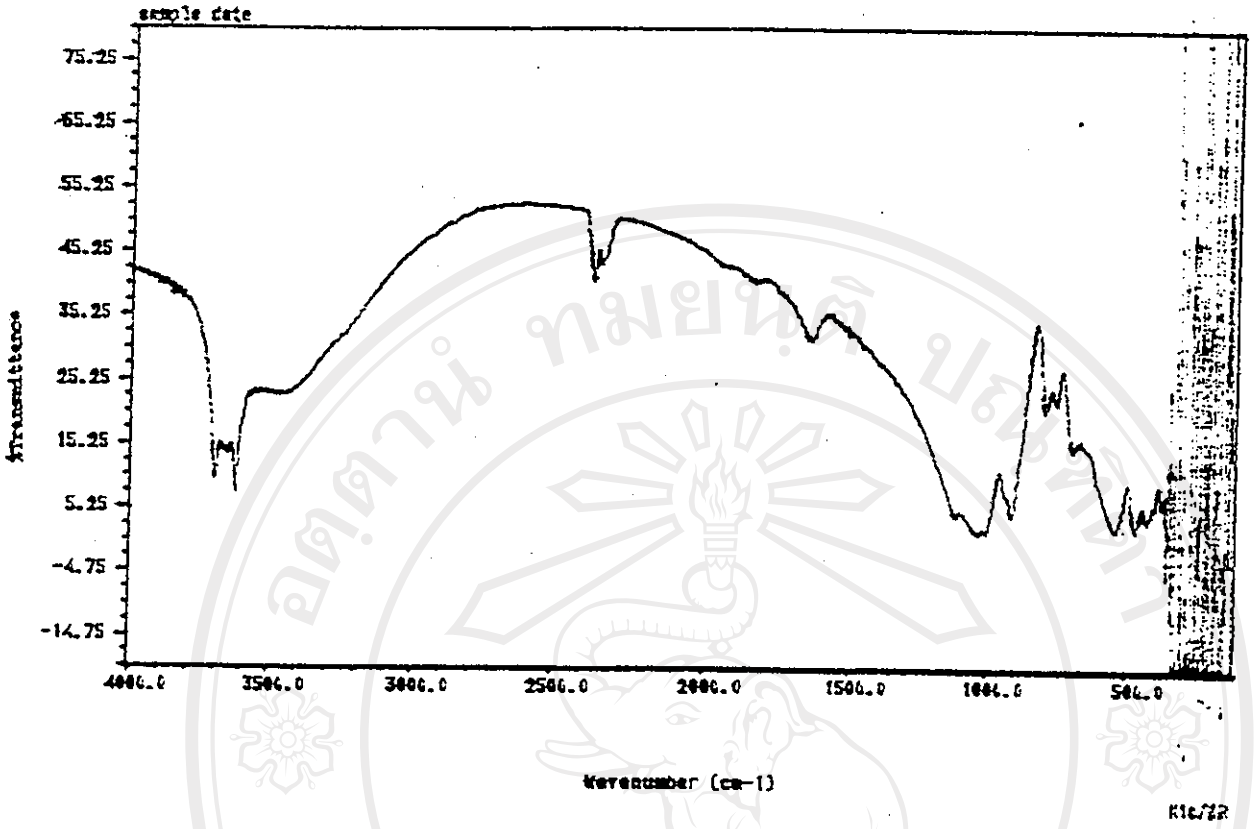

Fig. 3.37 Infrared spectrum of Co : BA at ratio 13.1 : 1

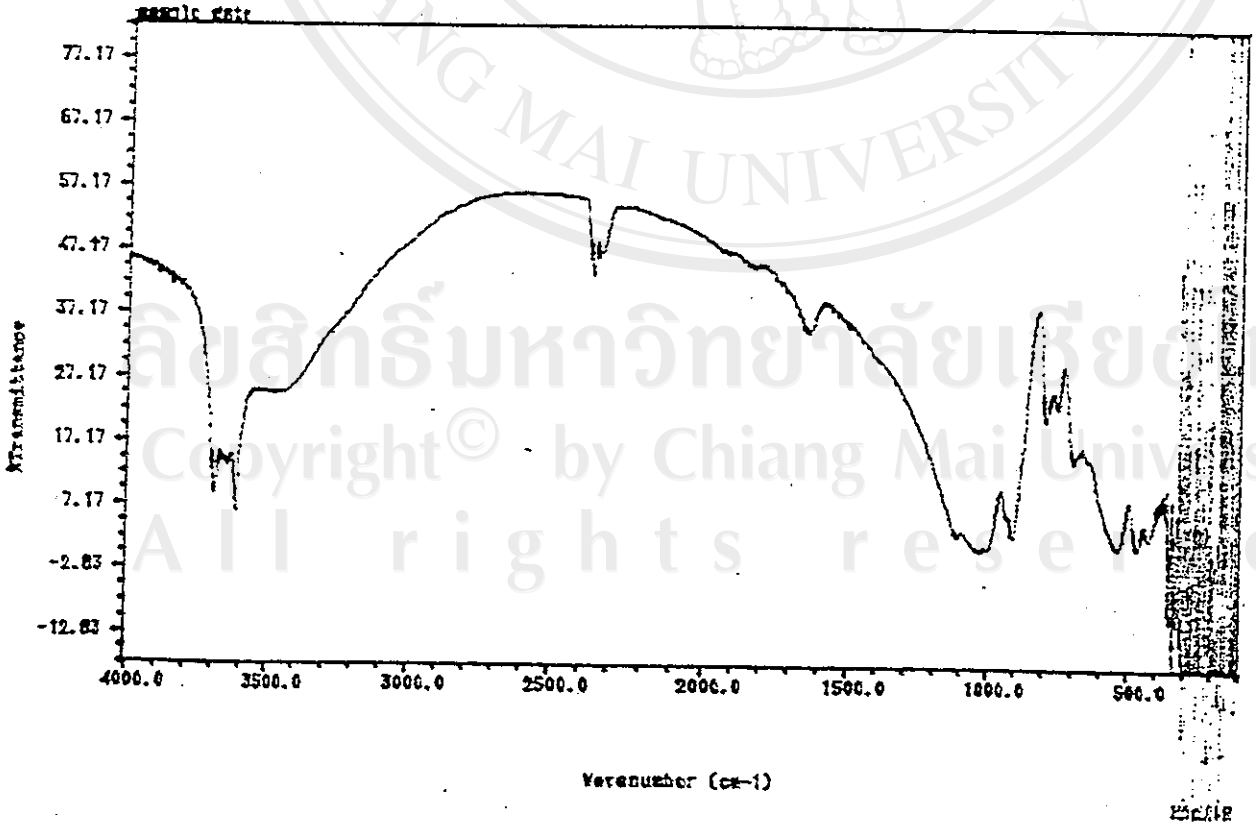

Fig. 3.38 Infrared spectrum of Co-bentonite with deionize water

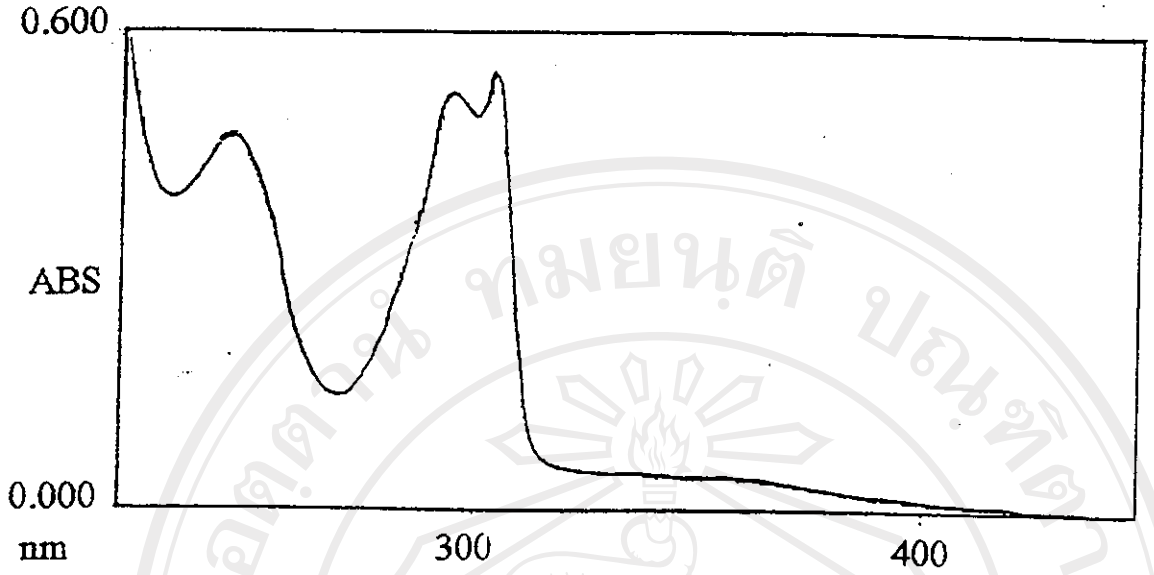

Fig. 3.39 Electronic spectrum of Ni : NH_3 at ratio 10.6 : 1

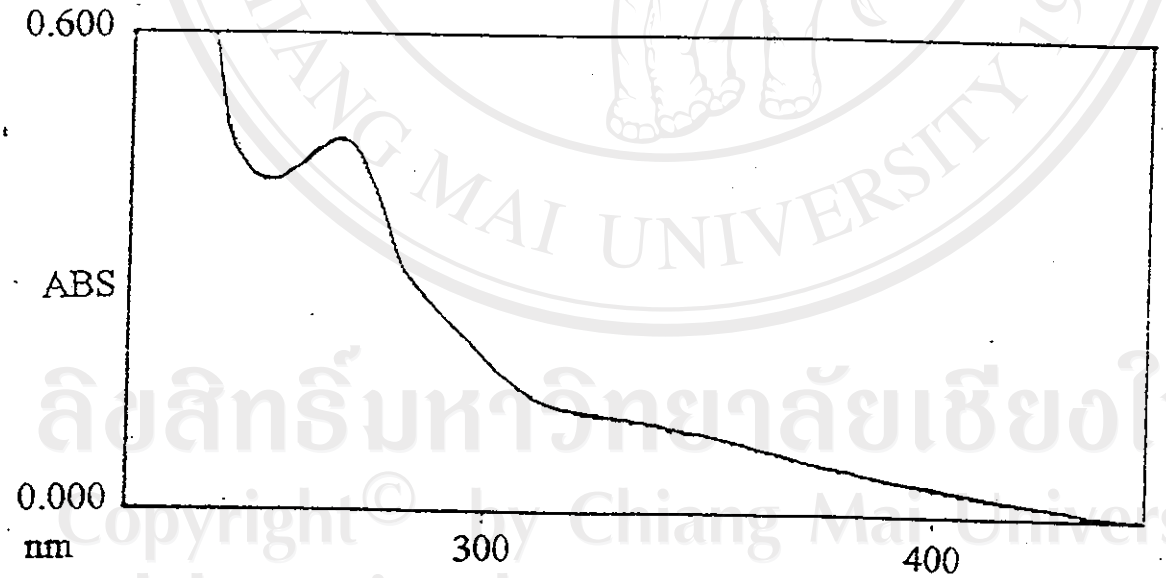

Fig. 3.40 Electronic spectrum of Ni : en at ratio 10.6 : 1

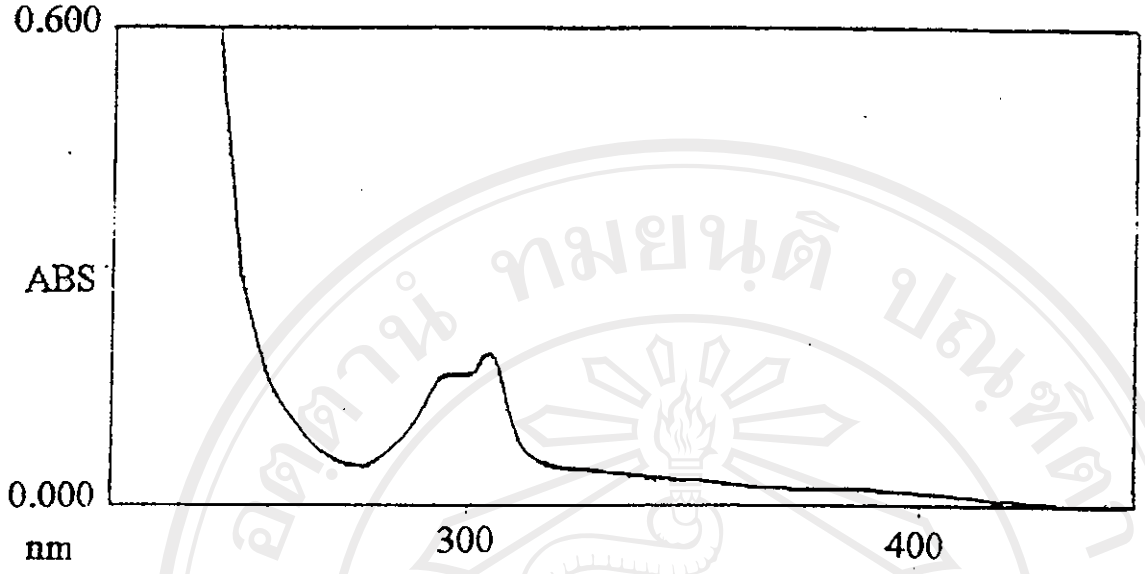

Fig. 3.41 Electronic spectrum of Ni : BA at ratio 10.6 : 1

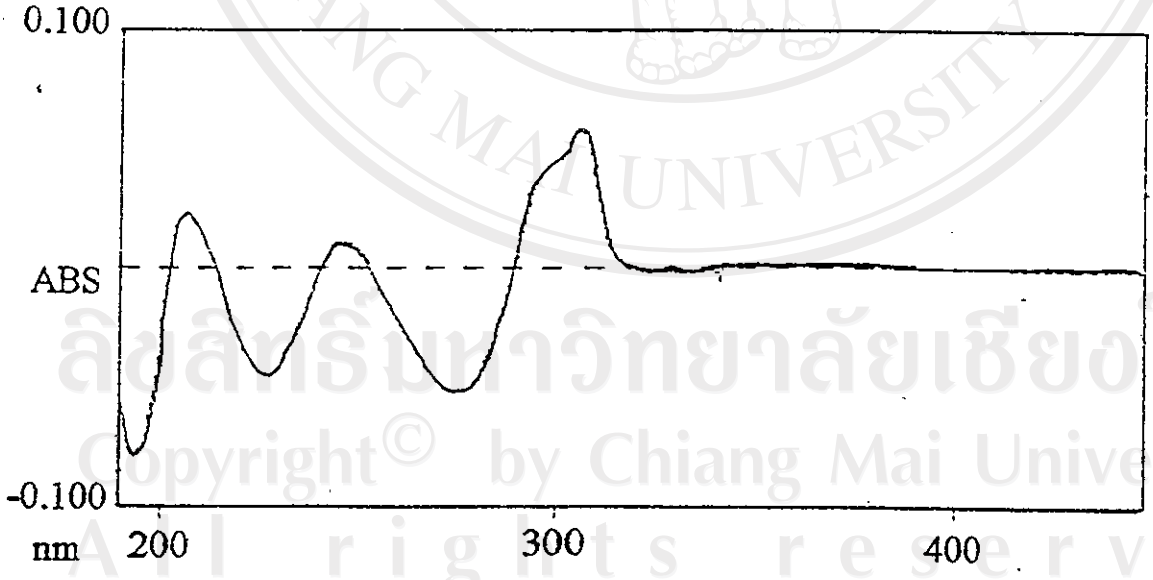

Fig. 3.42 Electronic spectrum of Ni-bentonite with deionize water

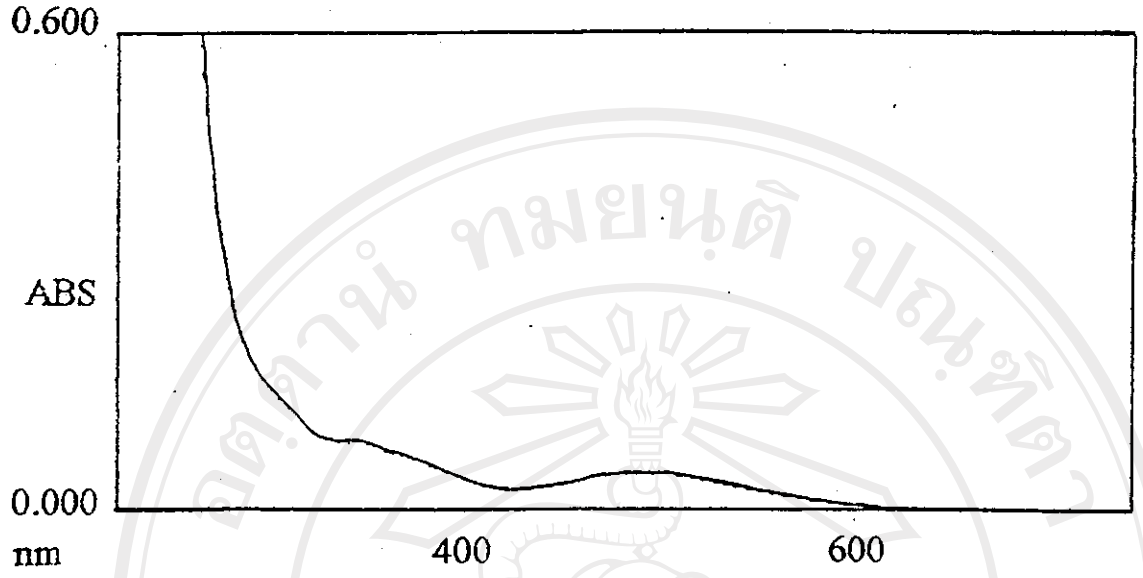

Fig. 3.43 Electronic spectrum of Co : NH_3 at ratio 13.1 : 1

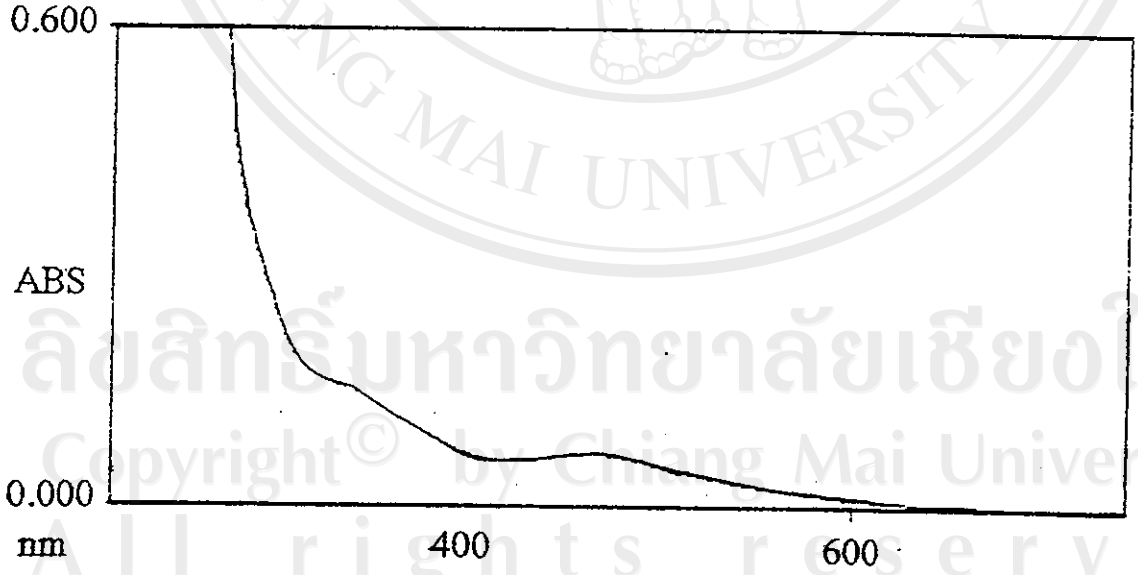

Fig. 3.44 Electronic spectrum of Co : en at ratio 13.1 : 1

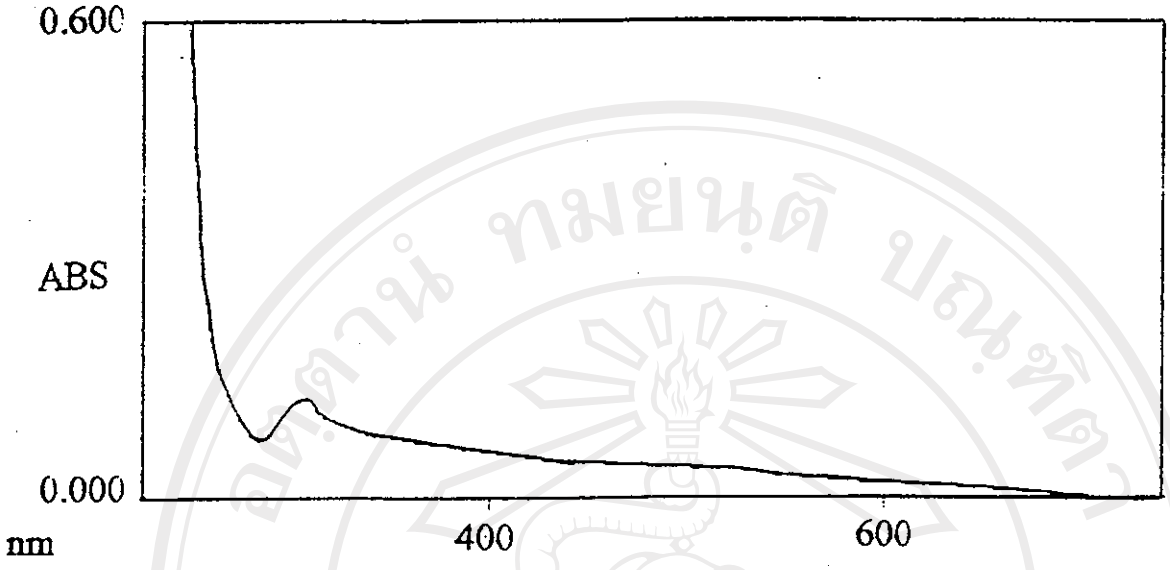

Fig. 3.45 Electronic spectrum of Co : BA at ratio 13.1 : 1

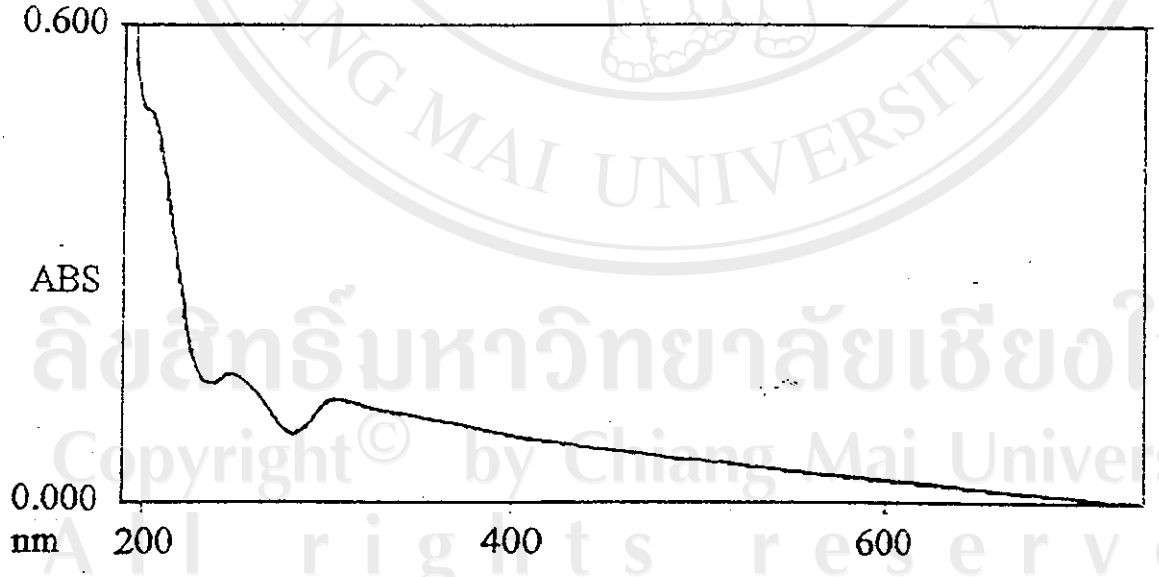

Fig. 3.46 Electronic spectrum of Co-bentonite with deionize water

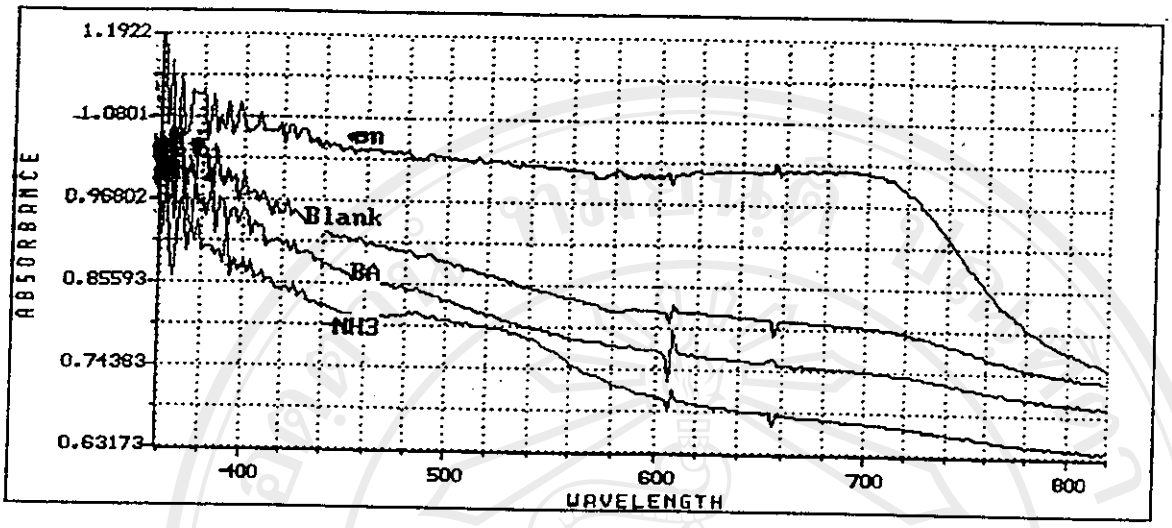

Fig. 3.47 Diffuse reflectance spectrum of Ni : ligand at equal concentration

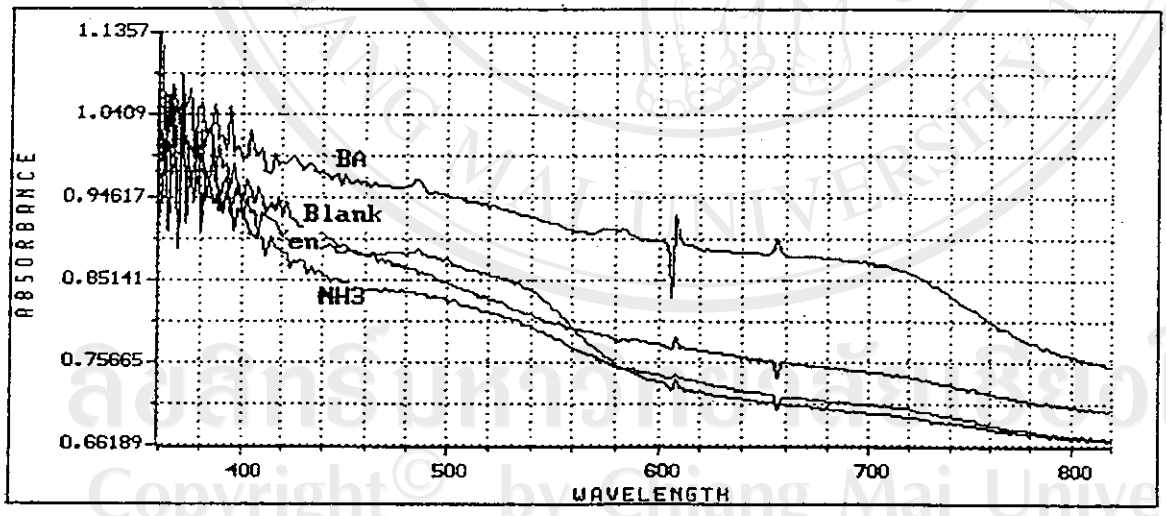

Fig. 3.48 Diffuse reflectance spectrum of Co : ligand at equal concentration

3.2.3.4 Reaction with various ligand concentration

The effect of differing metal / ligand ratios was explored, thus Ni-clay specimens(0.2 g) were added separately to solutions of ammonia(0.220, 0.022 and 0.002 M) and of butanoic acid(0.220, 0.022 and 0.002 M). The mixtures were stirred for 3 days and filtered. The solids were air-dried at room temperature, each clay specimen was examined by IR and diffuse relectance analysis. Liquids were retained for analysis.

In parallel experimentals, samples of the Co-bentonite(0.2 g) were treated with solutions of en (10 ml) (0.220, 0.022 and 0.002 M) and butanoic acid(0.220, 0.022 and 0.002 M). Results were given in Table 3.23 and Table 3.24.

Table 3.23 Physical characteristics of Ni-bentonite clay samples after treatement with organic ligand solutions at various concentration

Organic added	Ni/ligand ratio	colour of solid product
NH_3	1 : 3	green
NH_3	5 : 1	green
NH_3	50 : 1	green
BA	1 : 3	pink
BA	5 : 1	pink
BA	50 : 1	brown

Table 3.24 Physical characteristics of Co-bentonite clay samples after treatement with organic ligand solutions at various concentration

Organic added	Co / ligand ratio	colour of solid product
.en	1 : 3	brown
en	5 : 1	brown
en	50 : 1	pink
BA	1 : 3	pink
BA	5 : 1	pink
BA	50 : 1	pink

Table 3.25 Physical data from solutions remaining after treatement of Ni-bentonite clays with organic ligand solutions at various concentration

organic added	Ni / ligand ratio	colour of solution	Initial solution pH	Final solution pH	Ni released from clay mmole/1g	Percent Ni released
NH_3	1 : 3	pink	10.22	10.13	0.03	0.80
NH_3	5 : 1	pink	9.20	9.04	0.30	8.00
NH_3	50 : 1	pink	7.40	7.05	0.50	13.33
BA	1 : 3	-	3.00	3.22	3.75	100.00
BA	5 : 1	-	3.47	3.57	3.10	82.67
BA	50 : 1	-	4.15	4.36	2.20	58.67

Table 3.26 Physical data from solutions remaining after treatement of Co-bentonite clays with organic ligand solutions at various concentration

organic added	Ni / ligand ratio	colour of solution	Initial solution pH	Final solution pH	Ni released from clay mmole/1g	Percent Ni released
en	1 : 3	orange	11.02	10.88	1.30	43.33
en	5 : 1	orange	10.02	9.74	1.15	38.33
en	50 : 1	pink	6.84	6.50	0.95	31.67
BA	1 : 3	pink	3.04	2.82	2.65	88.33
BA	5 : 1	pink	3.74	3.62	2.30	76.67
BA	50 : 1	pink	4.26	4.29	2.15	71.67

3.2.3.5 Infrared spectra

The following absorption bands are characteristics of Ni-bentonite compounds shown in Table 3.27. IR spectra of Ni-bentonite were shown in Fig. 3.49-3.54 and Co-bentonite compounds were shown in Table 3.28 and Fig. 3.55-3.60.

Table 3.27 Physical characteristics of Ni-bentonite/1M after treatement with solution of organic ligands at various ligand concentrations

Ni/NH_3	Wavenumber(cm^{-1})	Assignments
1:3	3000(vw)	$\nu_s(NH_3)$
	1370(w)	$\delta_s(HNH)$
5:1	1370(w)	$\delta_s(HNH)$
50:1	3000(vw)	$\nu_s(NH_3)$
	1400(w)	$\delta_s(HNH)$
Ni/BA		
1:3	1800(vw)	$\nu_a(C=O)$
5:1	1800(vw)	$\nu_a(C=O)$
50:1	1800(vw)	$\nu_a(C=O)$

Table 3.28 Physical characteristics of Co-bentonite/1M after treatement with solution of organic ligands at various ligand concentrations

Co/en	Wavenumber(cm^{-1})	Assignments
1:3	3200(m)	ν_a(NH)
	3100(m)	ν_s(NH)
	2940(vw)	$\nu_s(CH_2)$
5:1	3200(m)	ν_a(NH)
	3100(m)	ν_s(NH)
	2940(vw)	$\nu_s(CH_2)$
50:1	3200(w)	ν_a(NH)
	3100(w)	ν_s(NH)
Co/BA		
1:3	1800(vw)	ν_a(C=O)
5:1	1800(vw)	ν_a(C=O)
50:1	1800(vw)	ν_a(C=O)

3.2.3.6 Electronic spectra

Ni-bentonite/1M and Co-bentonite/1M were contacted with various ratio of ligands; NH_3 and BA for nickel clay and en and BA for cobalt clay.

Result of solution electronic spectrum of Ni-bentonite/1M were in Fig.3.61-3.66 and of solid spectrum in Fig. 3.73-3.74. Absorption peaks were listed in Table. 3.29-3.30. Co-bentonite/1M solution spectra shown in Fig.3.67-3.72. Fig. 3.75-3.76 shown solid spectra of the compounds and absorption peaks were listed in Table 3.31-3.32.

Table 3.29 Peaks derived from electronic spectrum of Ni-bentonite/1M treated with various ratio of organic ligands in solution

Organic added	Absorption peaks of filtrate solution(nm)	Complex	Ref.
NH_3 1:3	342(vw),304(m), 295(m)	$[Ni(H_2O)_6]^{2+}$, $NiCl_4^{2-}$	15, 12
NH_3 5:1	341(vw),306(m), 294(m)	$[Ni(H_2O)_6]^{2+}$, $NiCl_4^{2-}$	15, 12
NH_3 50:1	341(vw),305(m), 296(m)	$[Ni(H_2O)_6]^{2+}$, $NiCl_4^{2-}$	15, 12
BA 1:3,5:1,50:1	305(m),296(m)	$NiCl_4^{2-}$	12

Table 3.30 Peaks derived from electronic spectrum of Ni-bentonite/1M treated with various ratio of organic ligands on clay

Organic added	Absorption peaks of solid clay(nm)	Complex	Ref.
NH_3 1:3,5:1,50:1	700(w-vw)	$[Ni(H_2O)_6]^{2+}$	15
BA 1:3,5:1,50:1	700(s)	$[Ni(H_2O)_6]^{2+}$	15

Table 3.31 Peaks derived from electronic spectrum of Co-bentonite/1M treated with various ratio of organic ligands in solution

Organic added	Absorption peaks of filtrate solution(nm)	Complex	Ref.
en 1:3	468(w),341(sh)	$Coen_3^{3+}$	18,19
en 5:1	470(w),342(sh)	$Coen_3^{3+}$	18,19
en 50:1	470(vw),341(vw),	$Coen_3^{3+}$	18,19
BA 1:3,5:1,50:1	303(w)	-	-

Table 3.32 Peaks derived from electronic spectrum of Co-bentonite/1M treated with various ratio of organic ligands on clay surface

Organic added	Absorption peaks of solid clay(nm)	Complex	Ref.
en 1:3,5:1,50:1	700(m)	$CoCl_2$	21
BA 1:3,5:1,50:1	700(m)	$CoCl_2$	21

3.2.3.7 Lability of complex nickel(II) on bentonite

Ni-bentonite/1M (2.20 g) was added to an ethylene-diamine solution (100 ml, 0.16 mole) and stirred for 24 h. The suspension was then filtered and washed with distilled water (25 ml). The air-dried solids were crushed to a fine power prior to use in the following experiments.

Portions (0.2 g) of this Ni-compound clay were then added separately to solutions (10 ml) of NaCl (0.5, 0.110 and 0.022 M), $CaCl_2$ (0.5, 0.110 and 0.022 M) and $CuCl_2$ (0.5, 0.110 and 0.022 M). Blank experiments with deionized water were also carried out. The suspensions were stirred for 3 days, and filtered. Results from the physical investigation of clay specimens and liquids were given in Table 3.33.

Table 3.33 Nickel content and pH values of solution remaining after contacting Ni-bentonite with a number of inorganic salt solutions

Cation added	M^{n+}/ Ni ratio	initial solution pH	Final solution pH	Ni in final solution (mmole)	Percent Ni desorbed
Na	5:1	8.16	7.84	0.90	7.57
	1:1	8.25	8.11	0.33	2.73
	1:5	8.25	8.02	0.08	0.67
Ca	5:1	7.95	7.57	1.90	15.93
	1:1	7.79	7.65	1.42	11.90
	1:5	7.94	7.64	0.93	7.82
Cu	5:1	3.08	2.81	1.80	15.14
	1:1	3.79	3.55	1.51	12.70
	1:5	4.21	4.24	1.03	8.66
dw	-	8.57	8.45	0.03	0.21

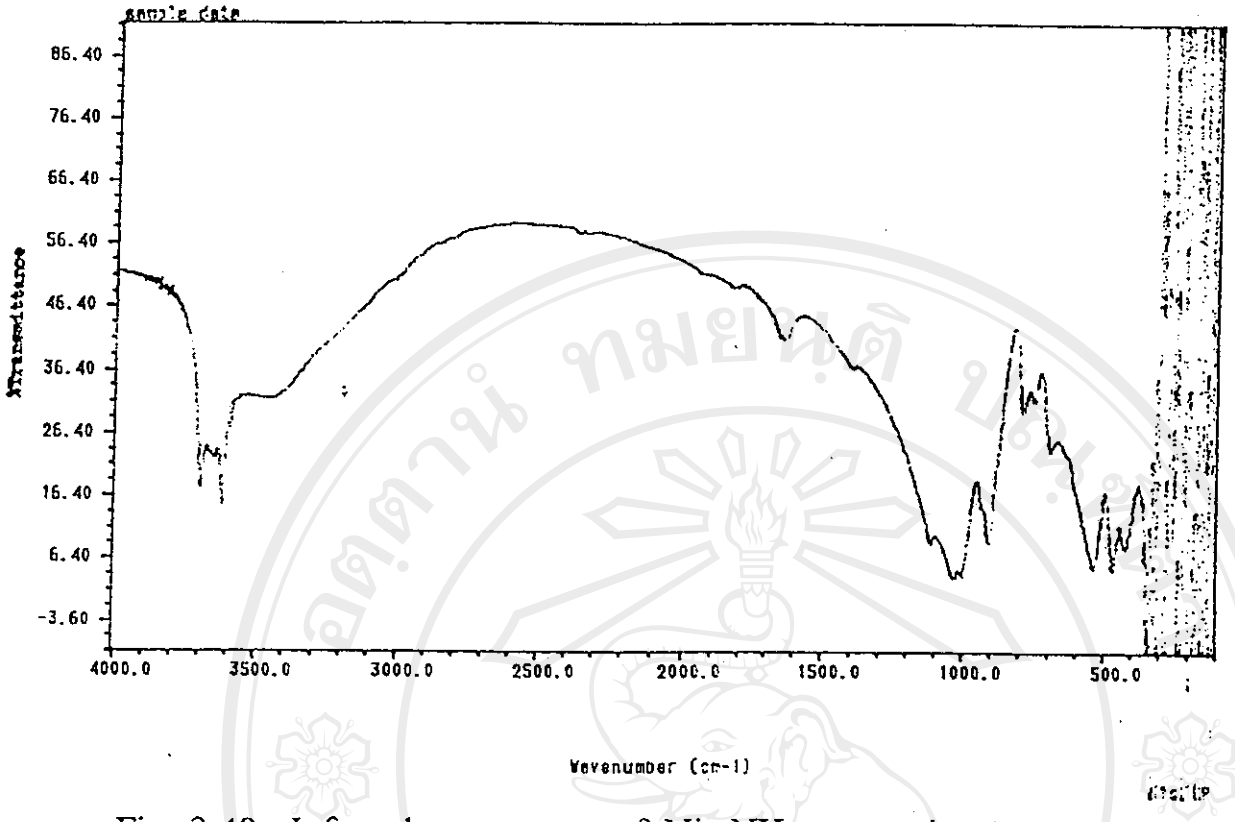

Fig. 3.49 Infrared spectrum of $Ni : NH_3$ at ratio 1 : 3

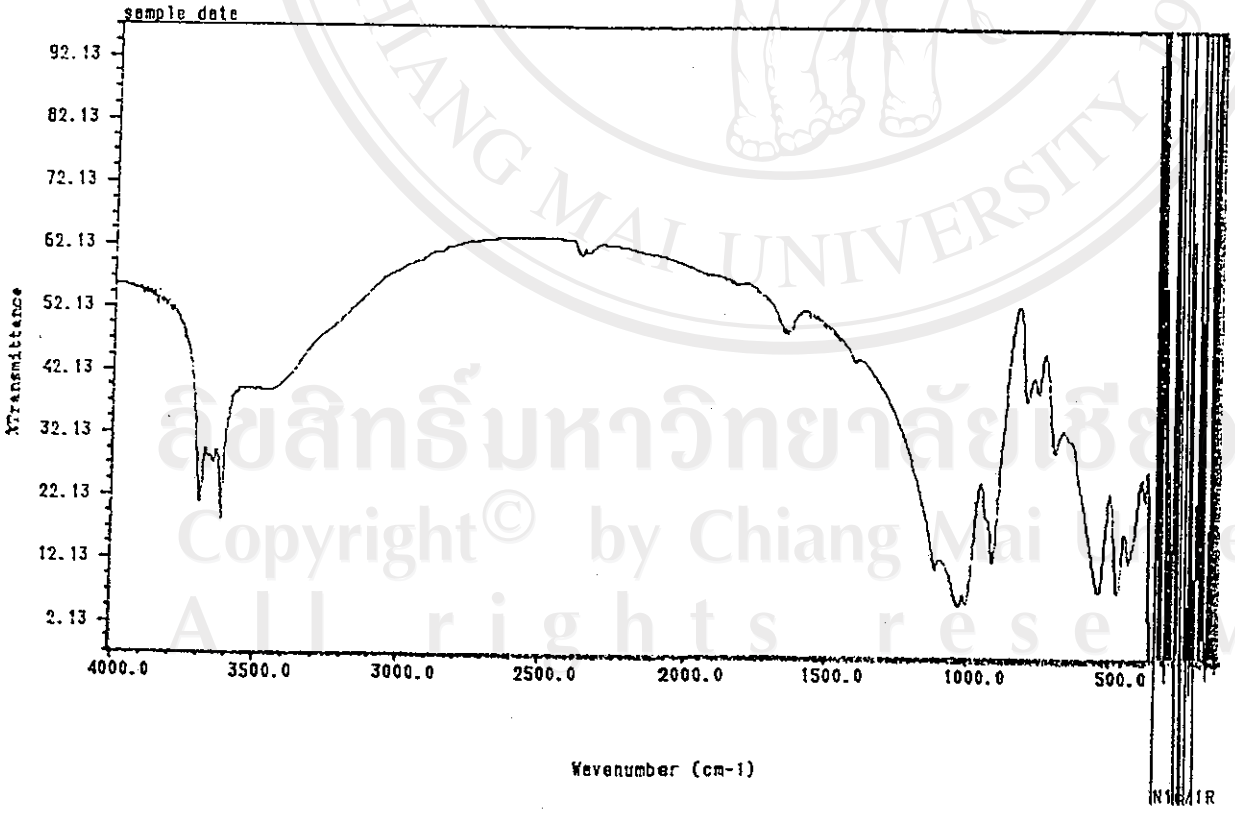

Fig. 3.50 Infrared spectrum of $Ni : NH_3$ at ratio 5 : 1

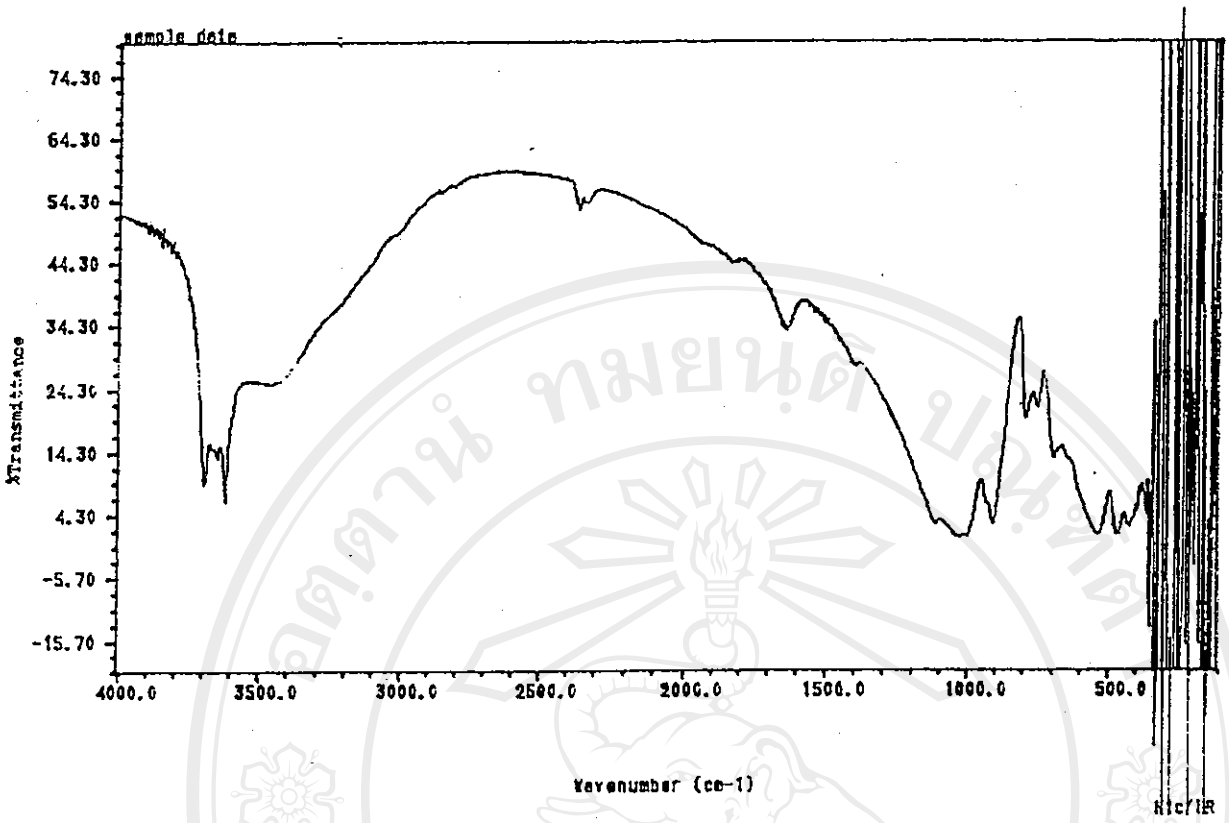

Fig. 3.51 Infrared spectrum of Ni : NH_3 at ratio 50 : 1

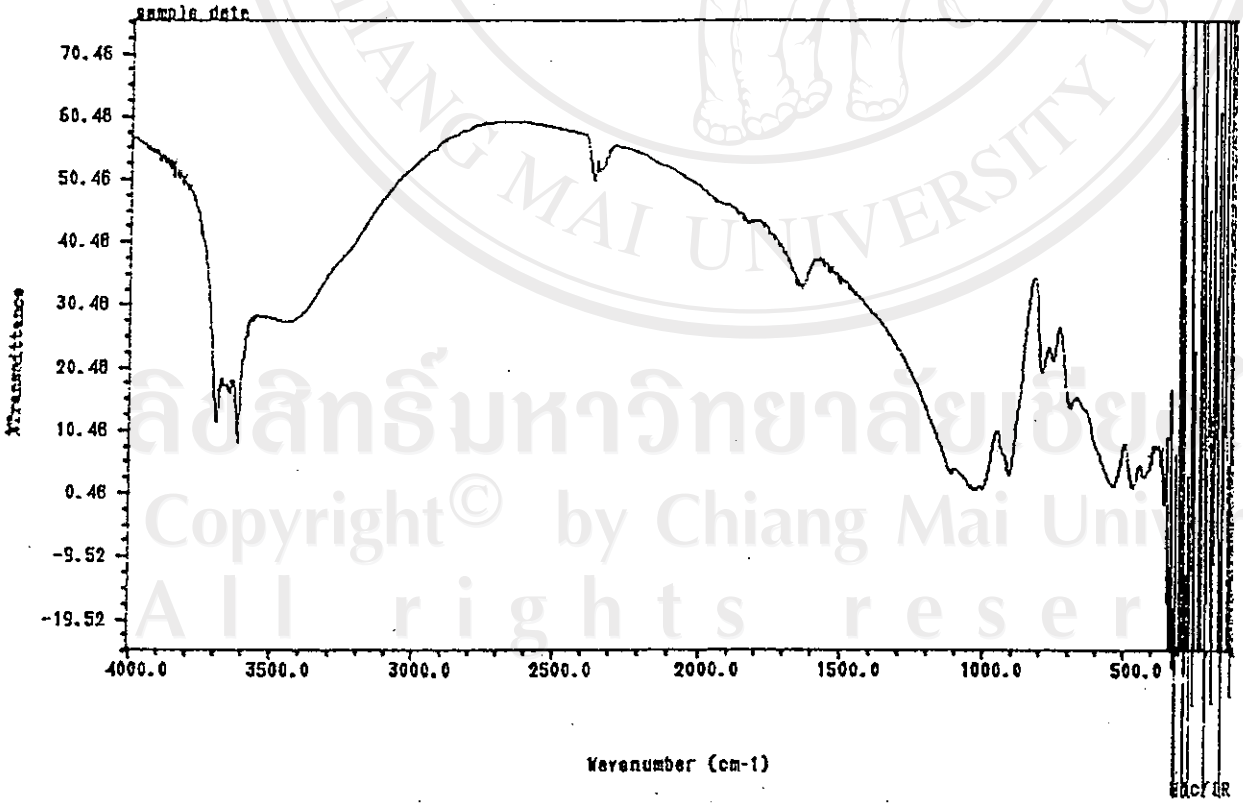

Fig. 3.52 Infrared spectrum of Ni : BA at ratio 1 : 3

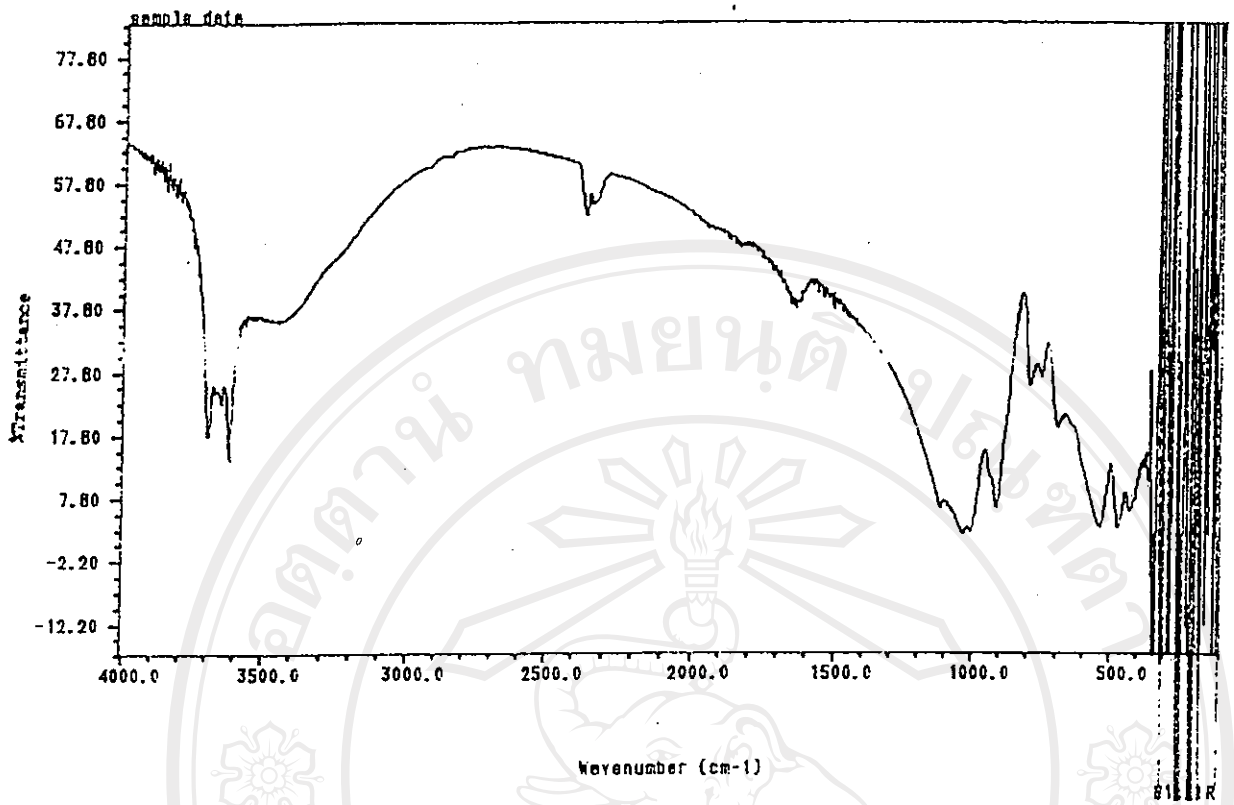

Fig. 3.53 Infrared spectrum of Ni : BA at ratio 5 : 1

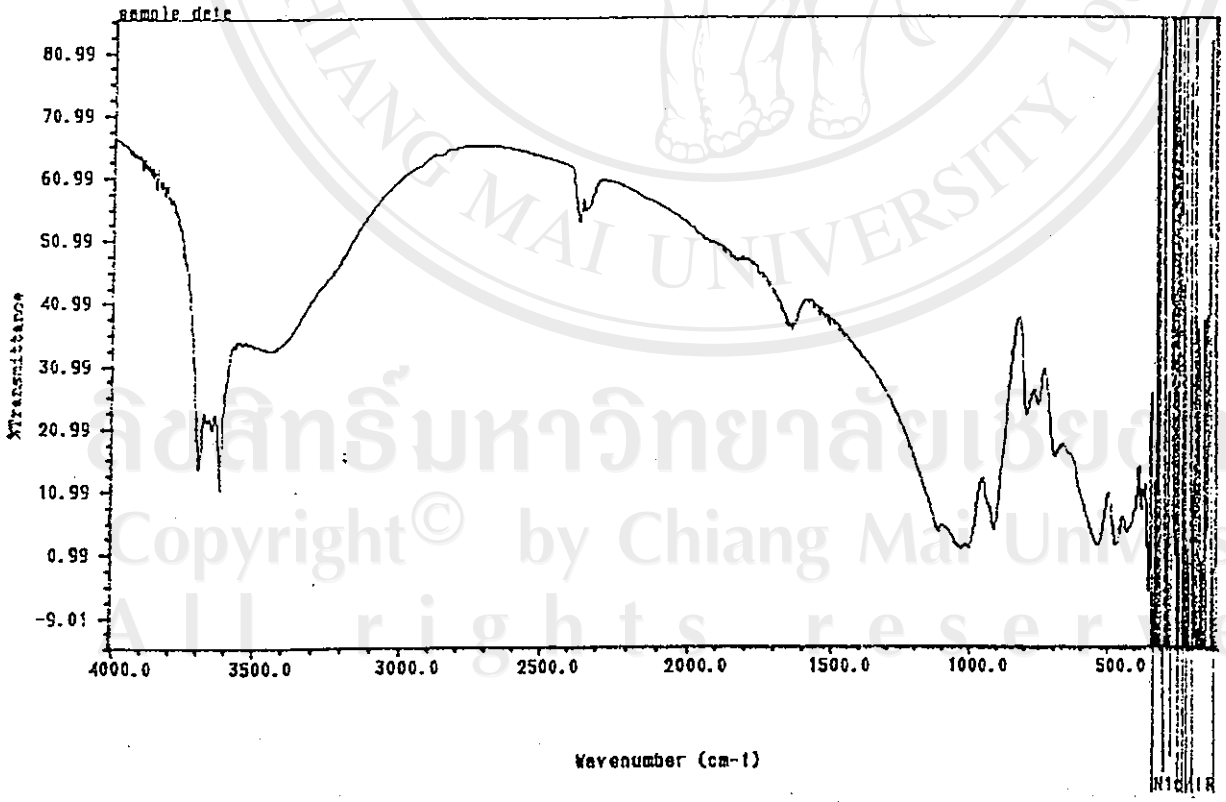

Fig. 3.54 Infrared spectrum of Ni : BA at ratio 50 : 1

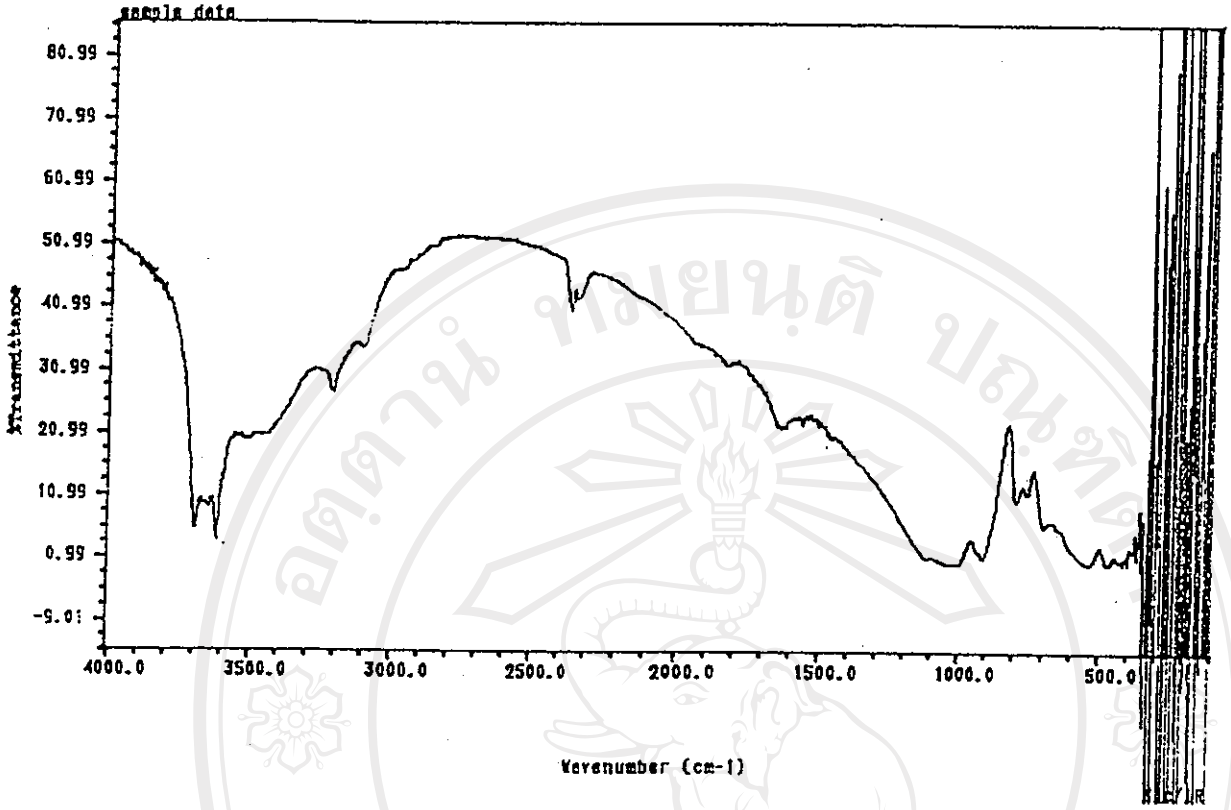

Fig. 3.55 Infrared spectrum of Co : en at ratio 1 : 3

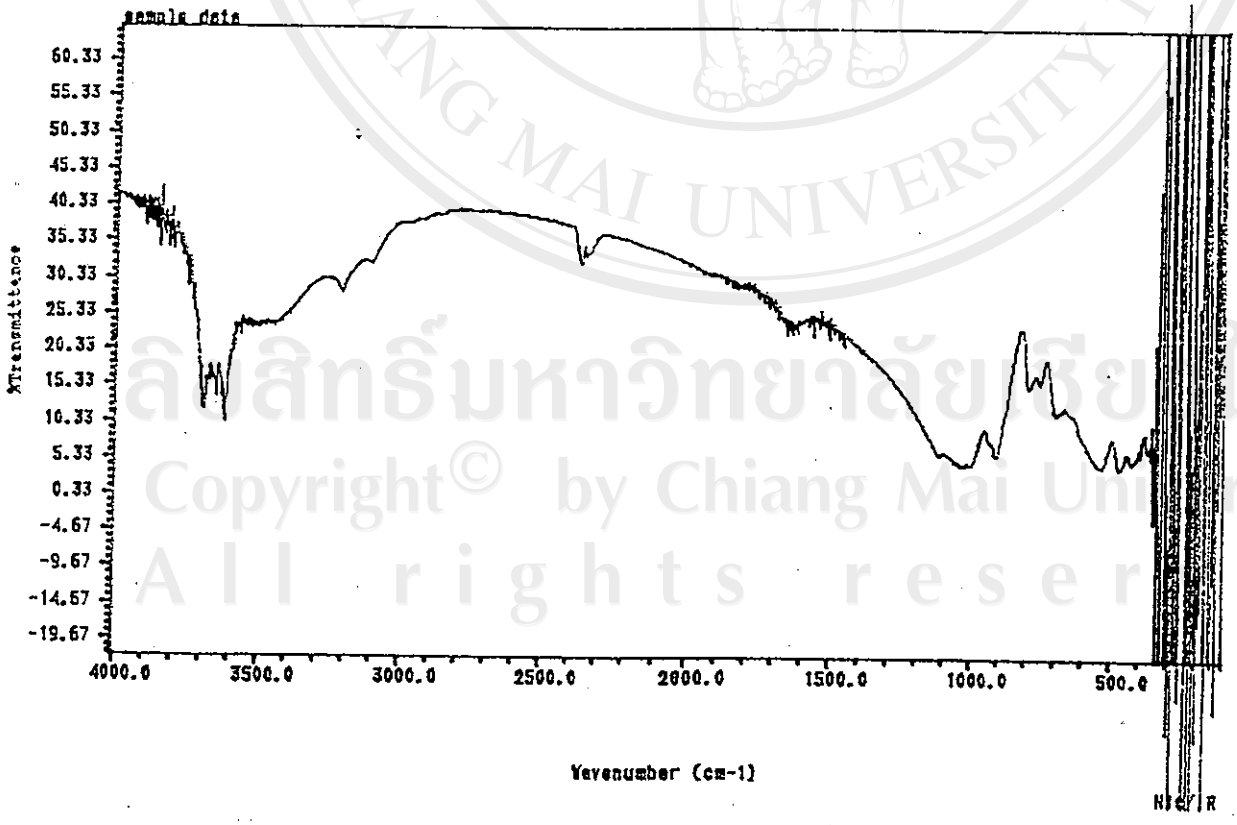

Fig. 3.56 Infrared spectrum of Co : en at ratio 5 : 1

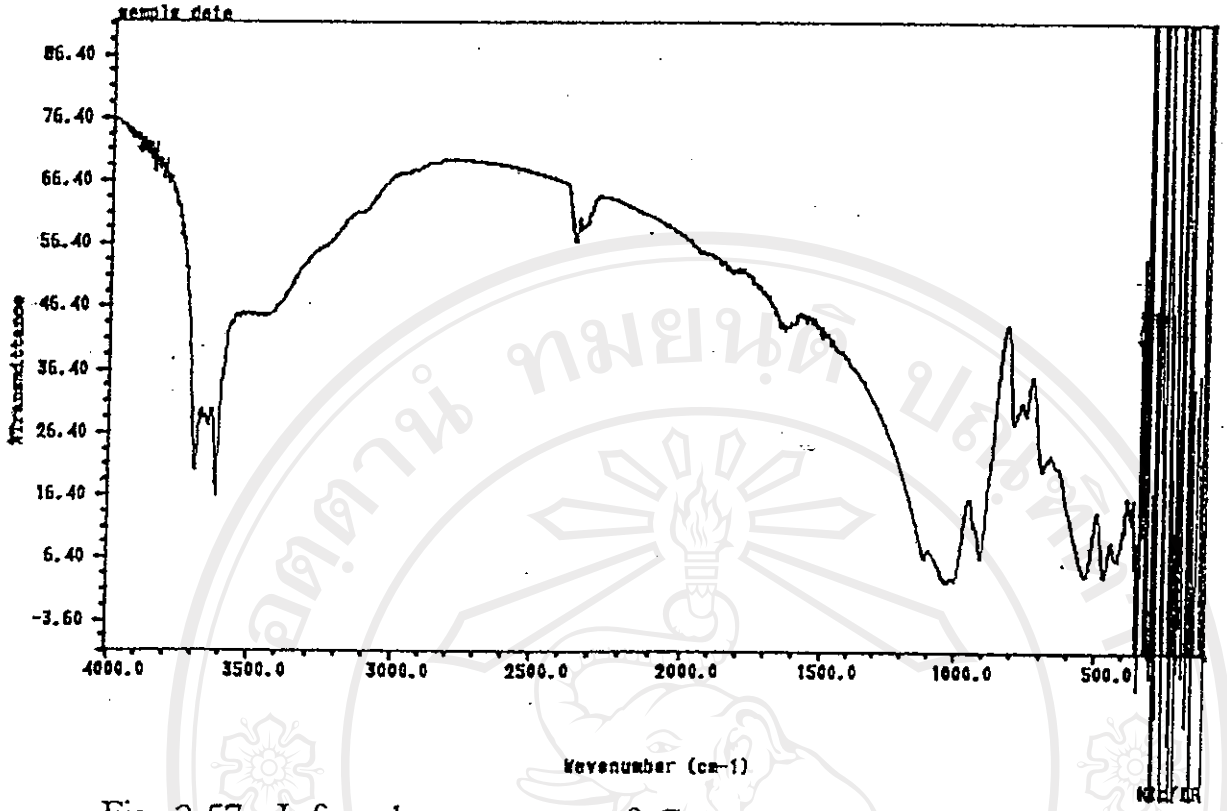

Fig. 3.57 Infrared spectrum of Co : en at ratio 50 : 1

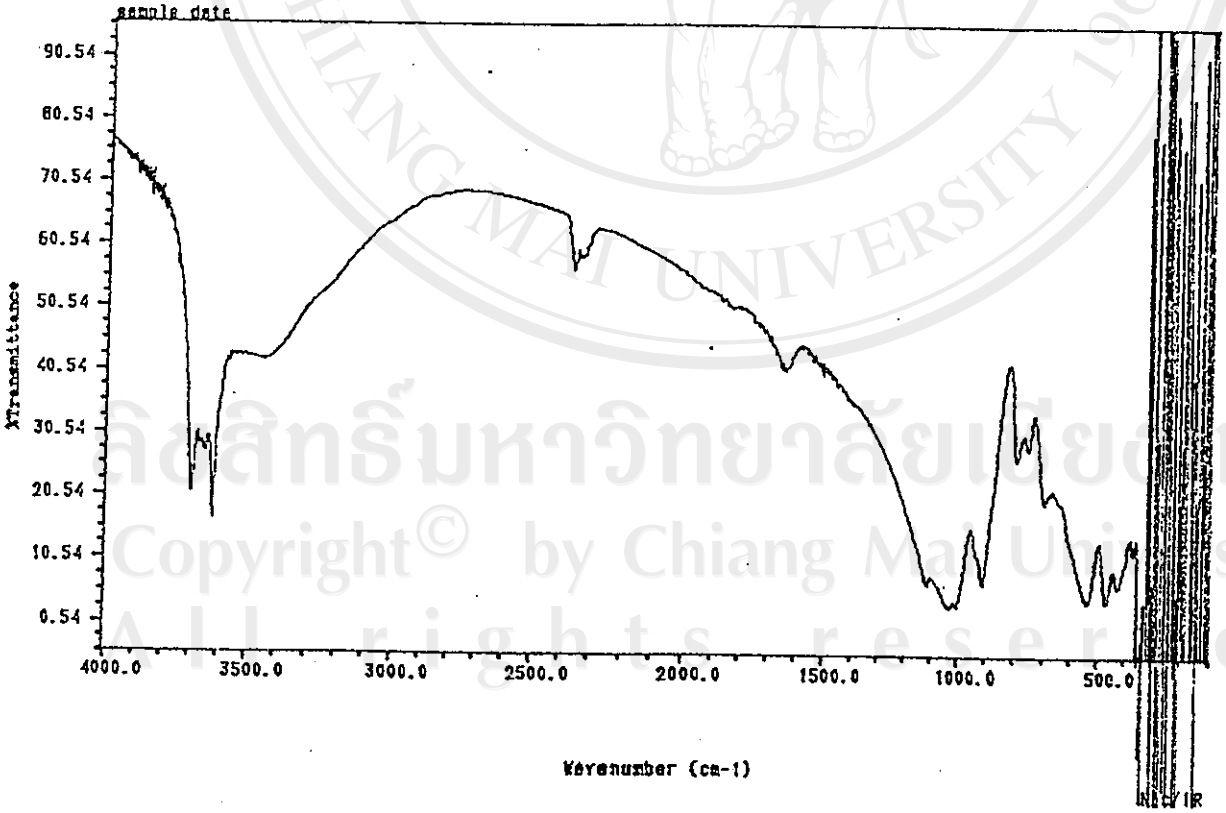

Fig. 3.58 Infrared spectrum of Co : BA at ratio 1 : 3

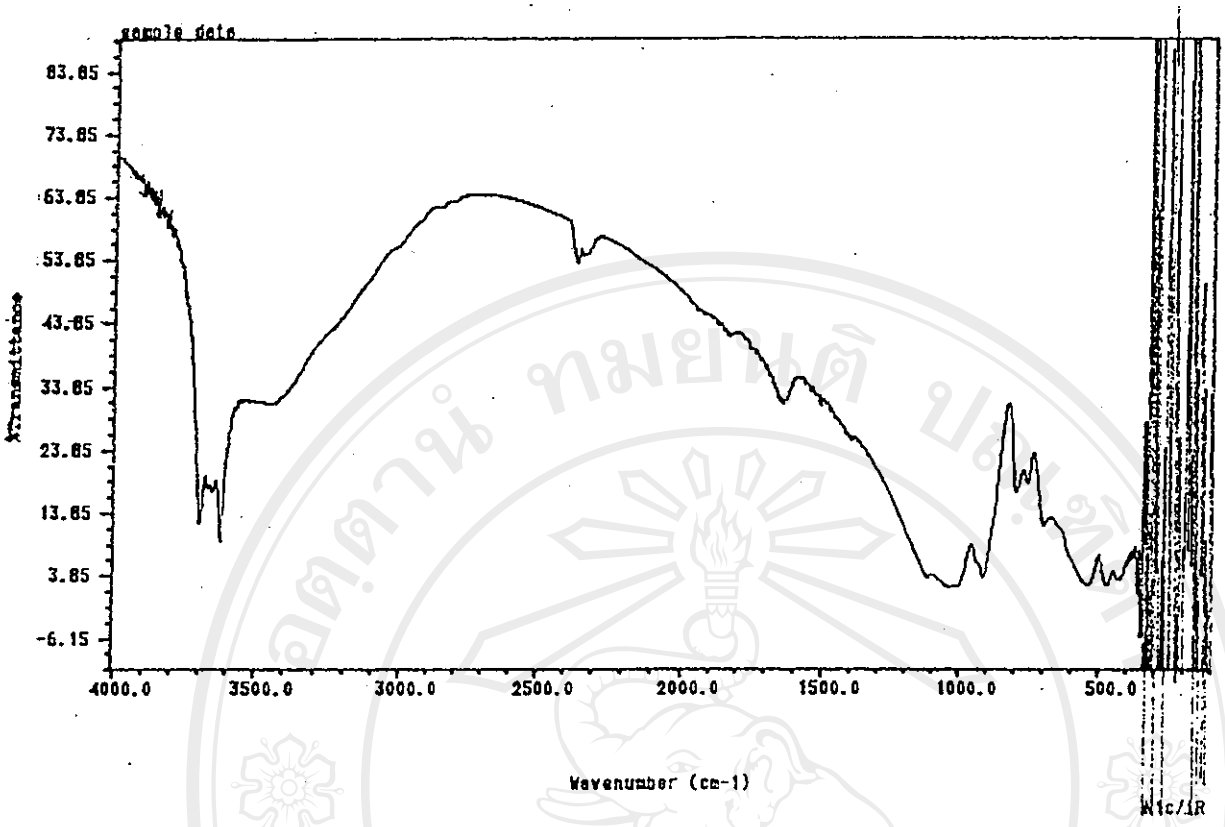

Fig. 3.59 Infrared spectrum of Co : BA at ratio 5 : 1

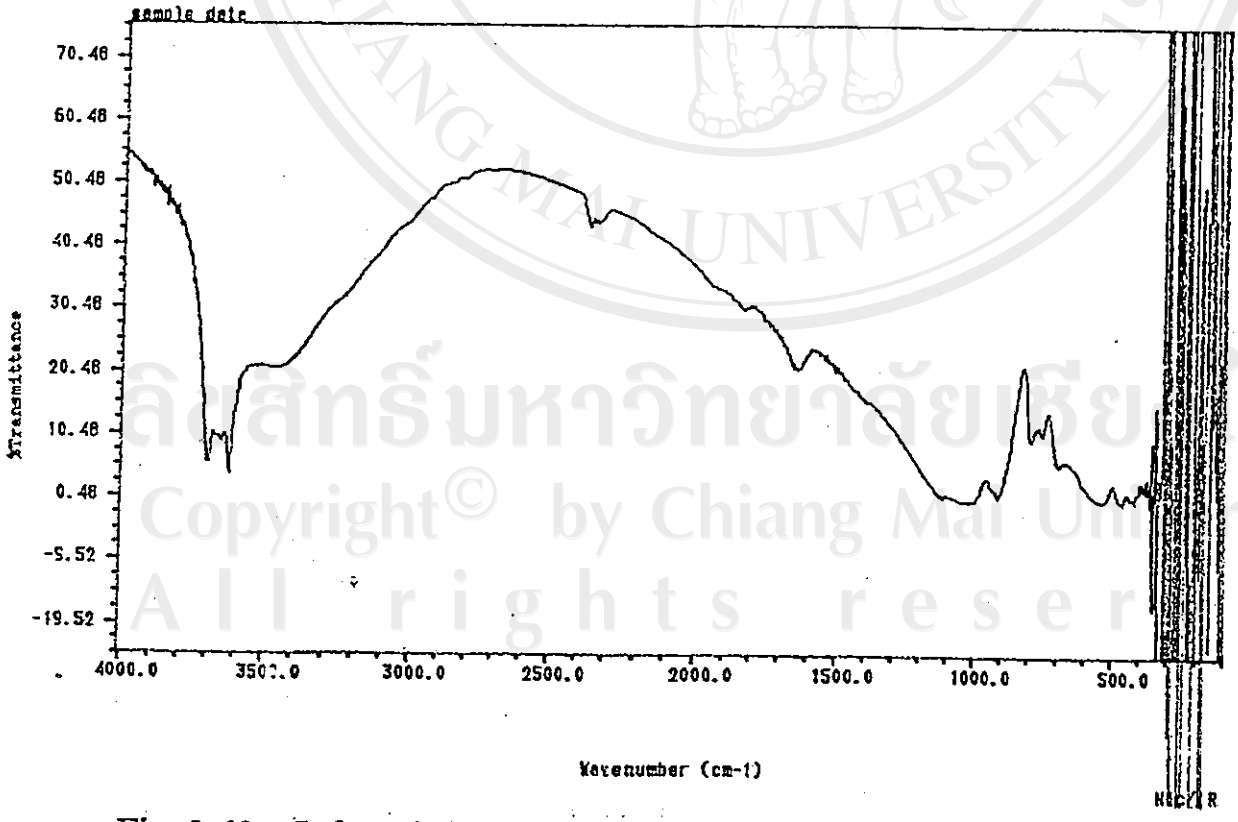

Fig. 3.60 Infrared spectrum of Co : BA at ratio 50 : 1

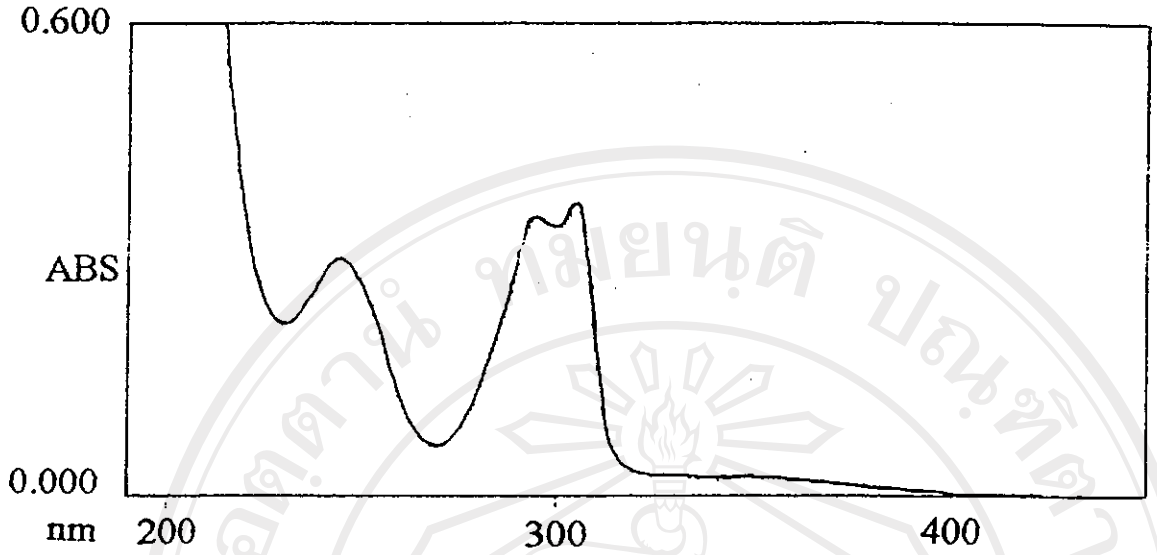

Fig. 3.61 Electronic spectrum of Ni : NH_3 at ratio 1 : 3

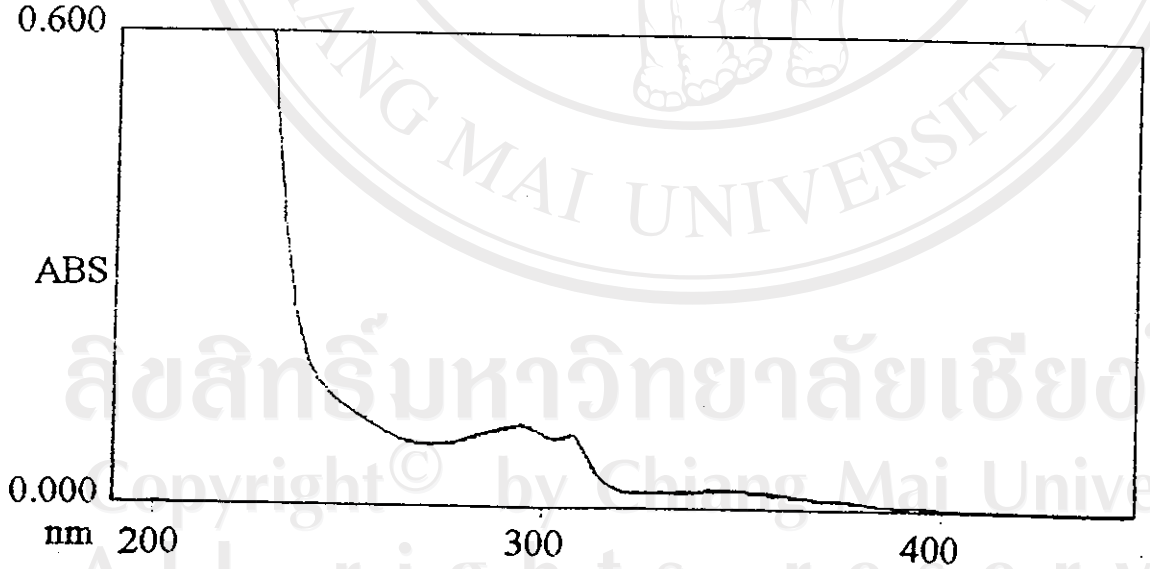

Fig. 3.62 Electronic spectrum of Ni : NH_3 at ratio 5 : 1

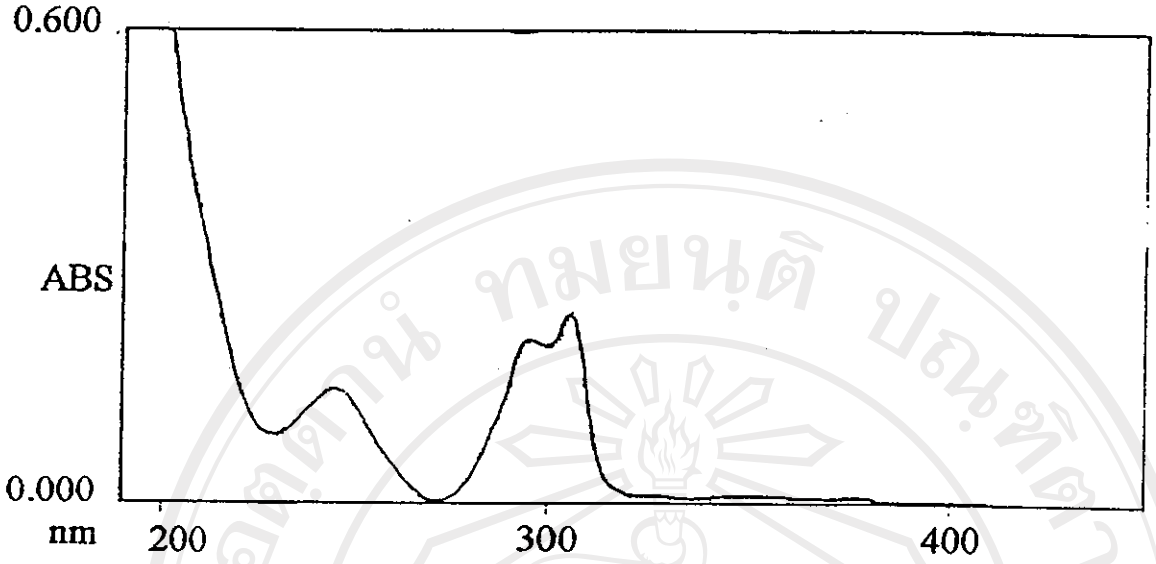

Fig. 3.63 Electronic spectrum of Ni : NH_3 at ratio 50 : 1

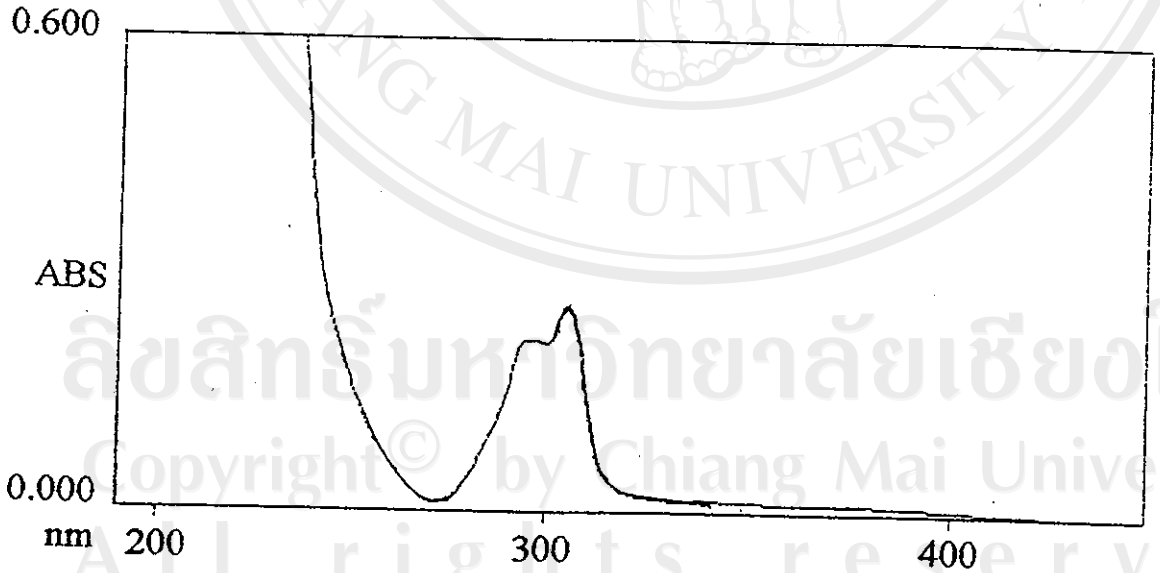

Fig. 3.64 Electronic spectrum of Ni : BA at ratio 1 : 3

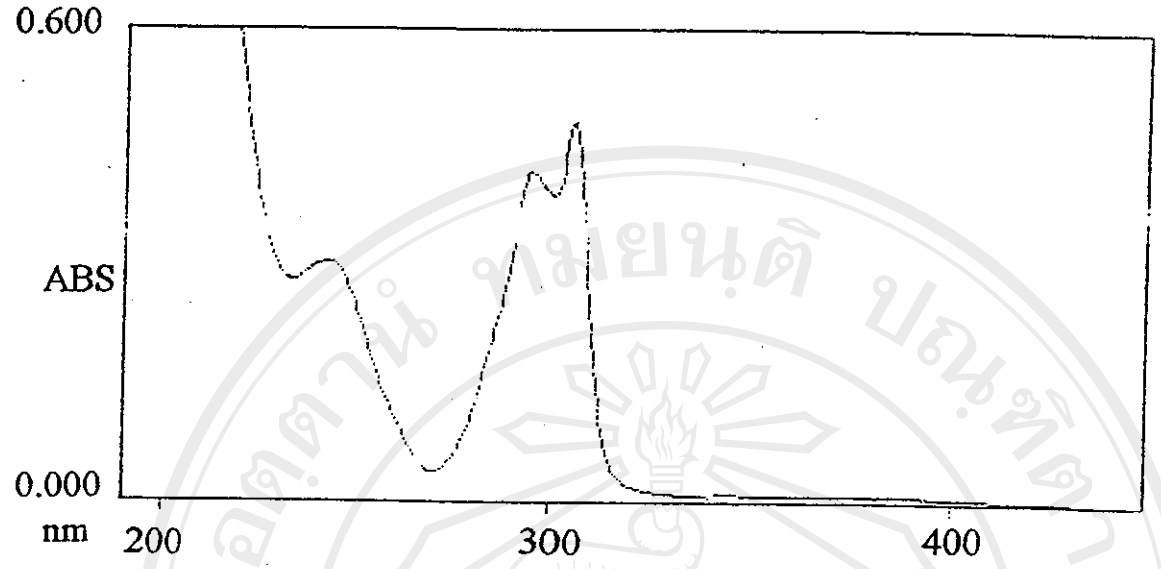

Fig. 3.65 Electronic spectrum of Ni : BA at ratio 5 : 1

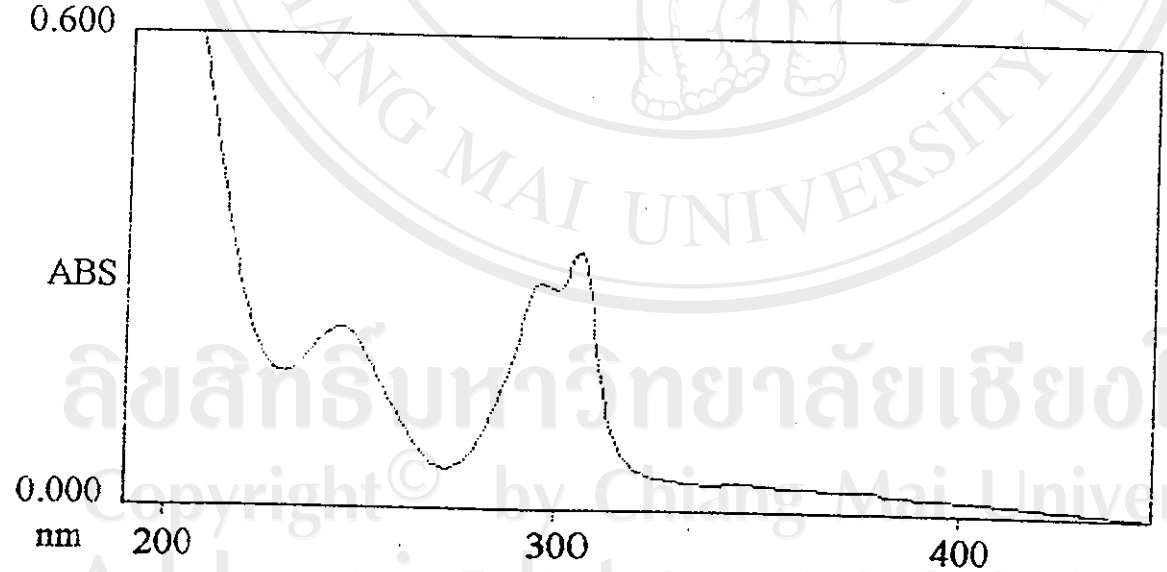

Fig. 3.66 Electronic spectrum of Ni : BA at ratio 50 : 1

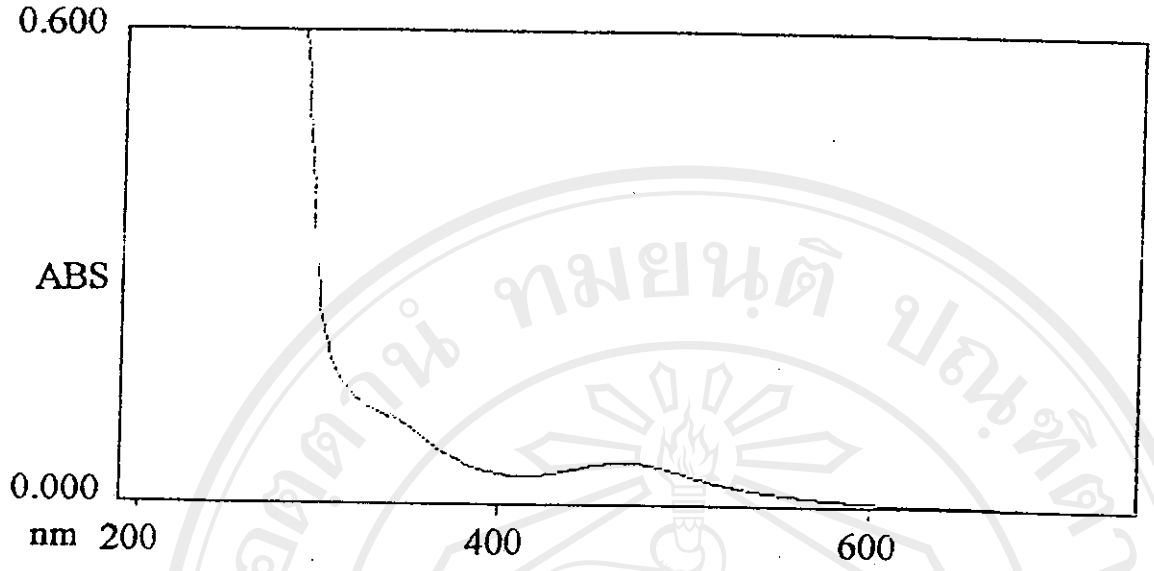

Fig. 3.67 Electronic spectrum of Co : en at ratio 1 : 3

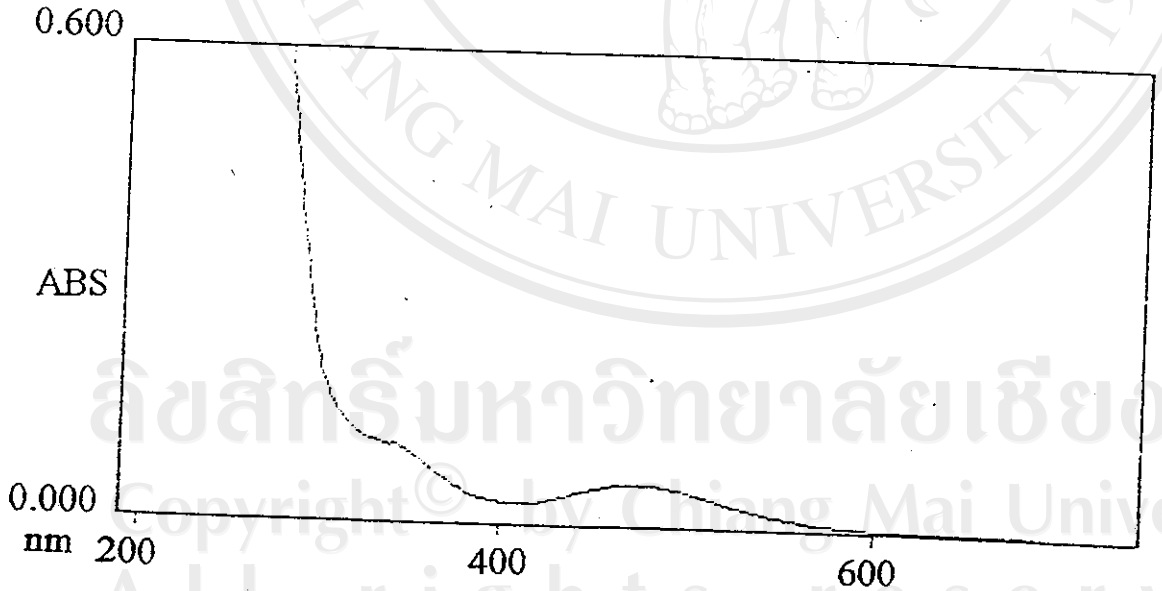

Fig. 3.68 Electronic spectrum of Co : en at ratio 5 : 1

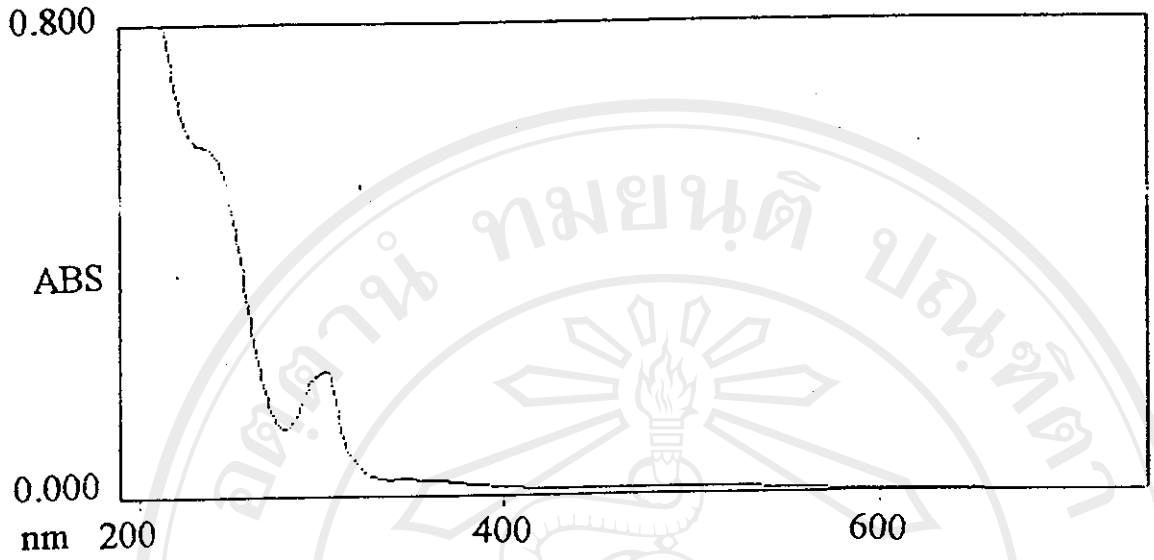

Fig. 3.69 Electronic spectrum of Co : en at ratio 50 : 1

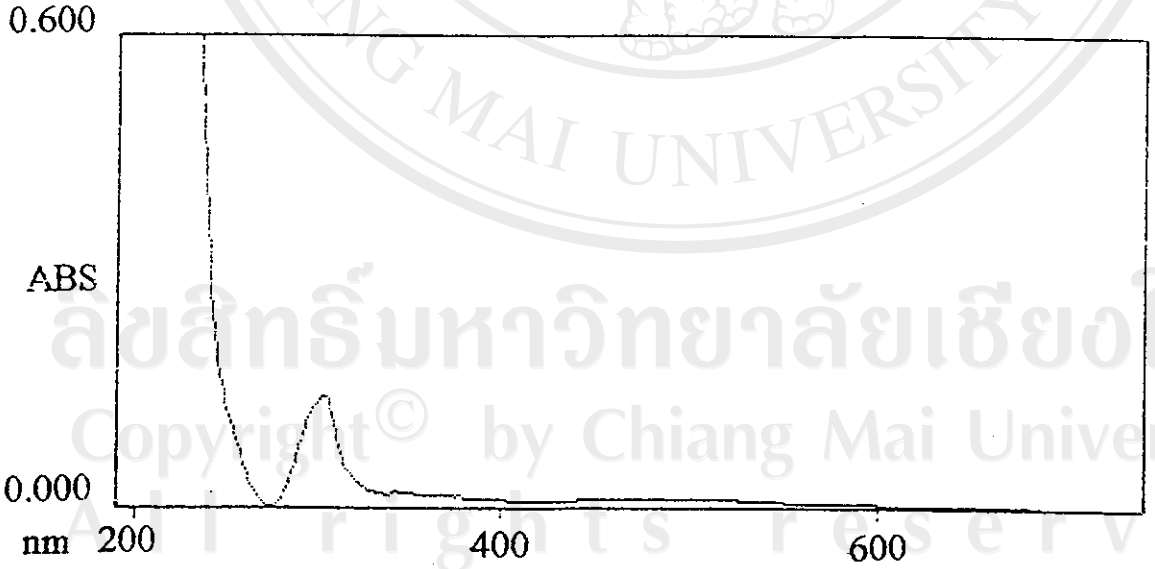

Fig. 3.70 Electronic spectrum of Co : BA at ratio 1 : 3

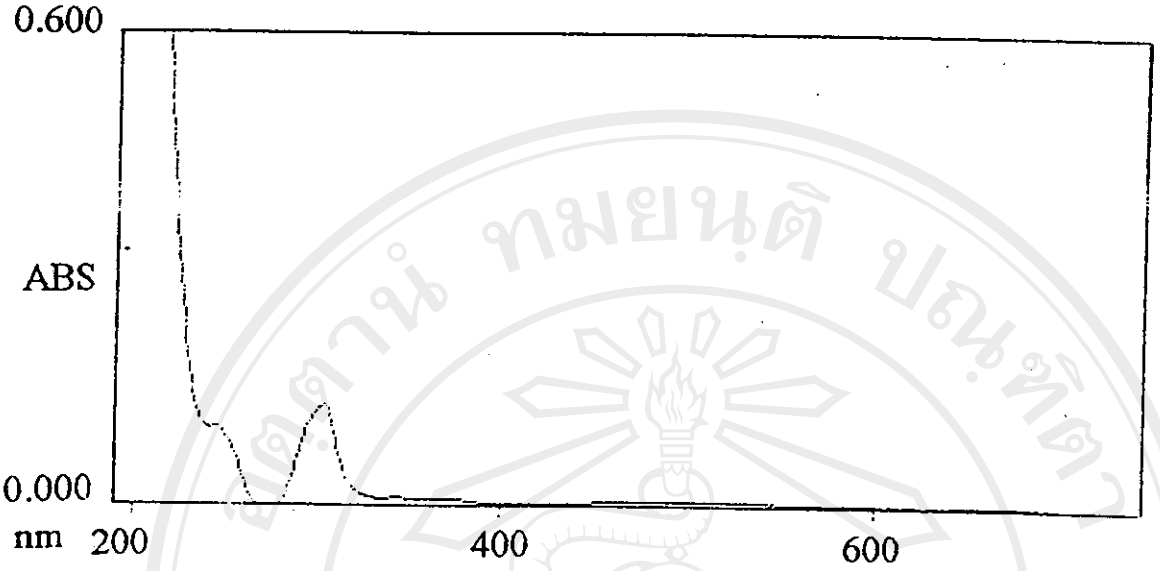

Fig. 3.71 Electronic spectrum of Co : BA at ratio 5 : 1

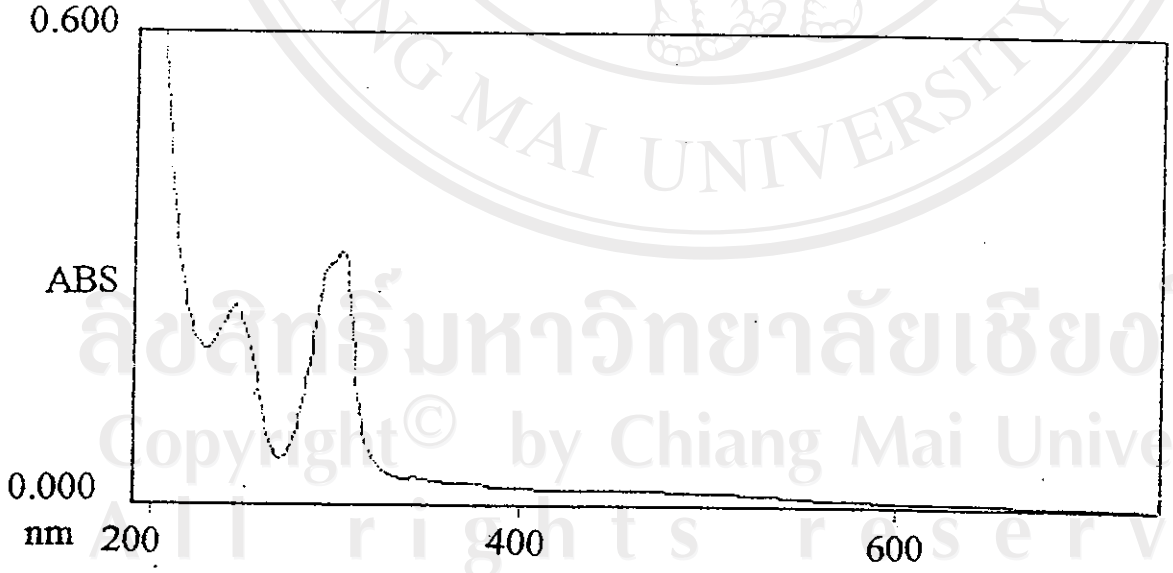

Fig. 3.72 Electronic spectrum of Co : BA at ratio 50 : 1

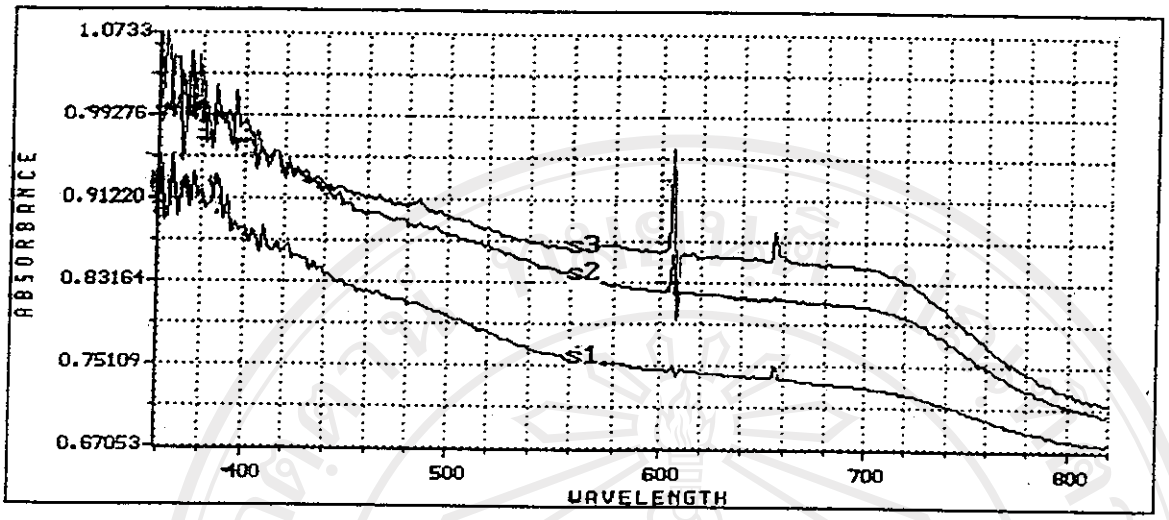

Fig. 3.73 Diffuse reflectance spectrum of Ni : NH_3 at various ratio s1=1:3 s2=5:1 s3=50:1

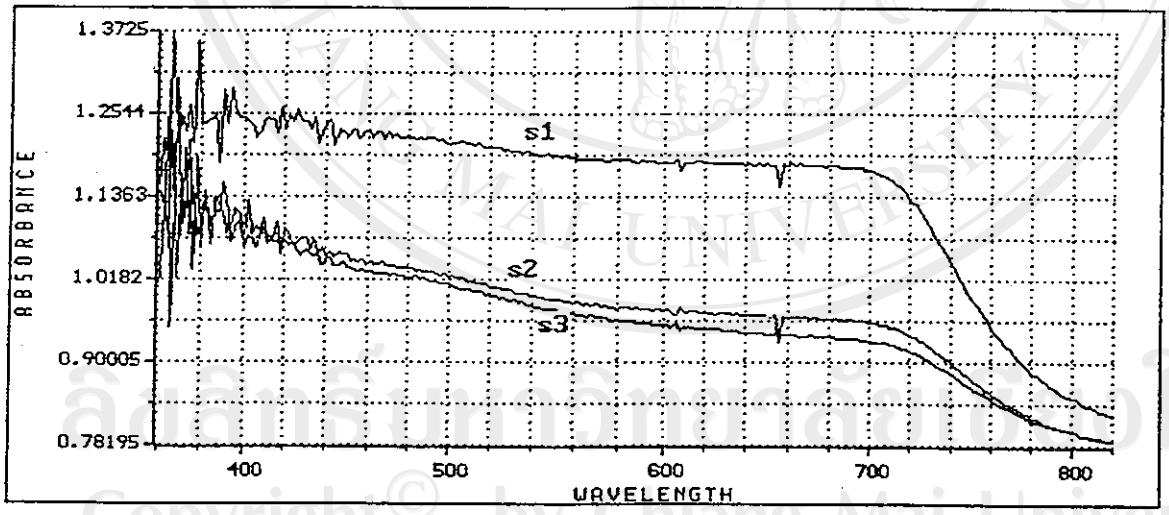

Fig. 3.74 Diffuse reflectance spectrum of Ni : BA at various ratio s1=1:3 s2=5:1 s3=50:1

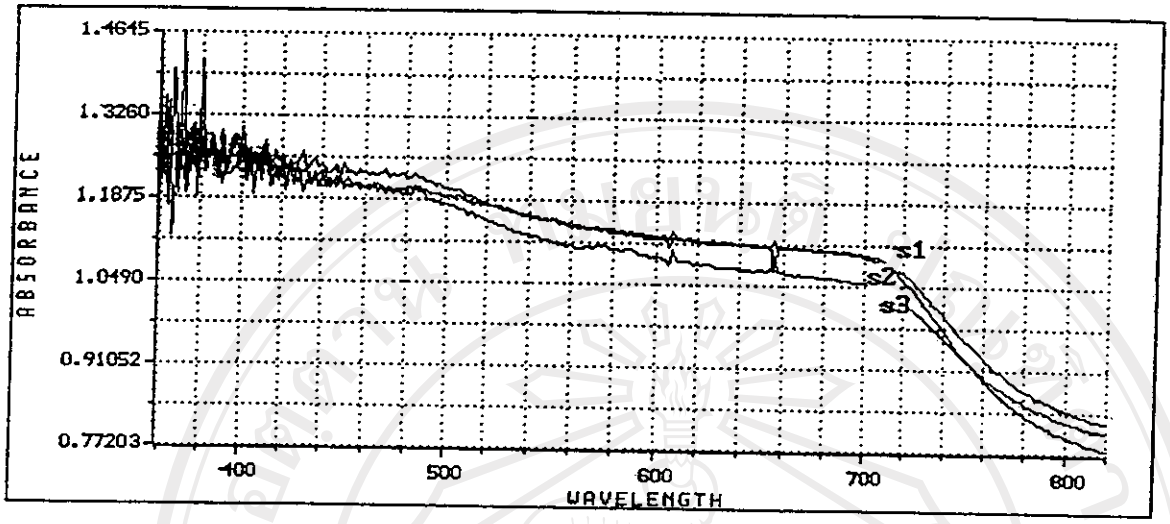

Fig. 3.75 Diffuse reflectance spectrum of Co : en at various ratio s1=1:3 s2=5:1 s3=50:1

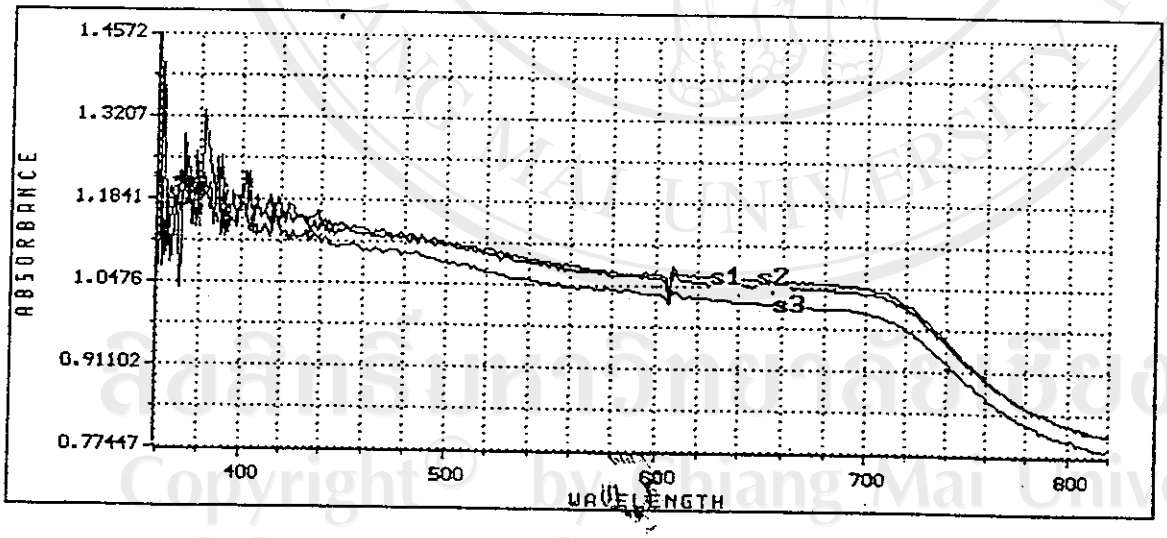

Fig. 3.76 Diffuse reflectance spectrum of Co : BA at various ratio s1=1:3 s2=5:1 s3=50:1

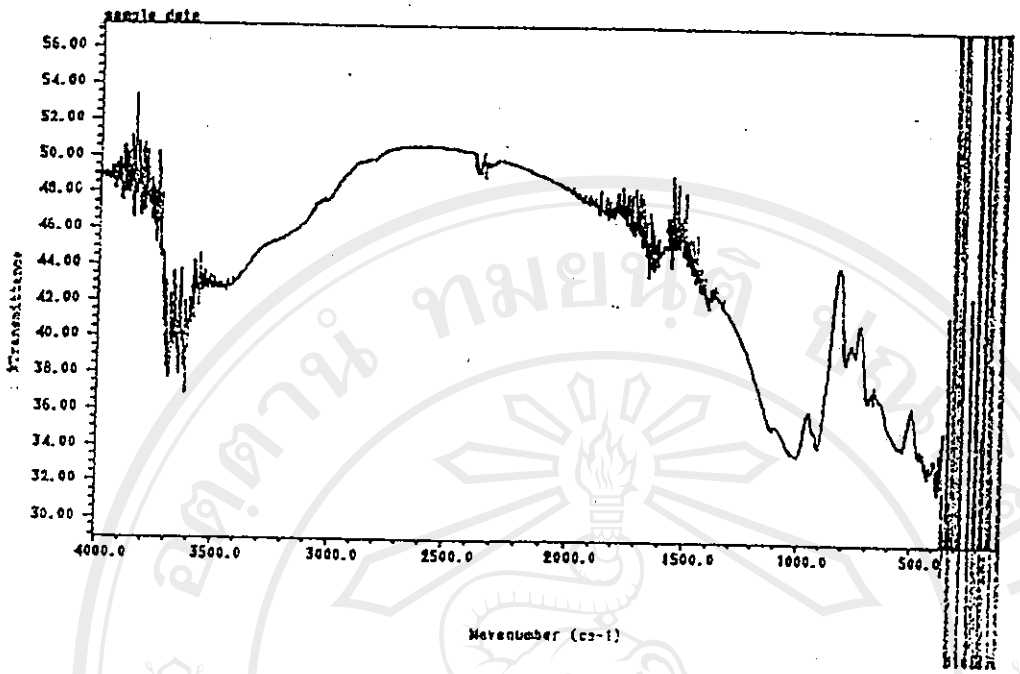

Fig. 3.77 Infrared spectrum of Ni : en -bentonite

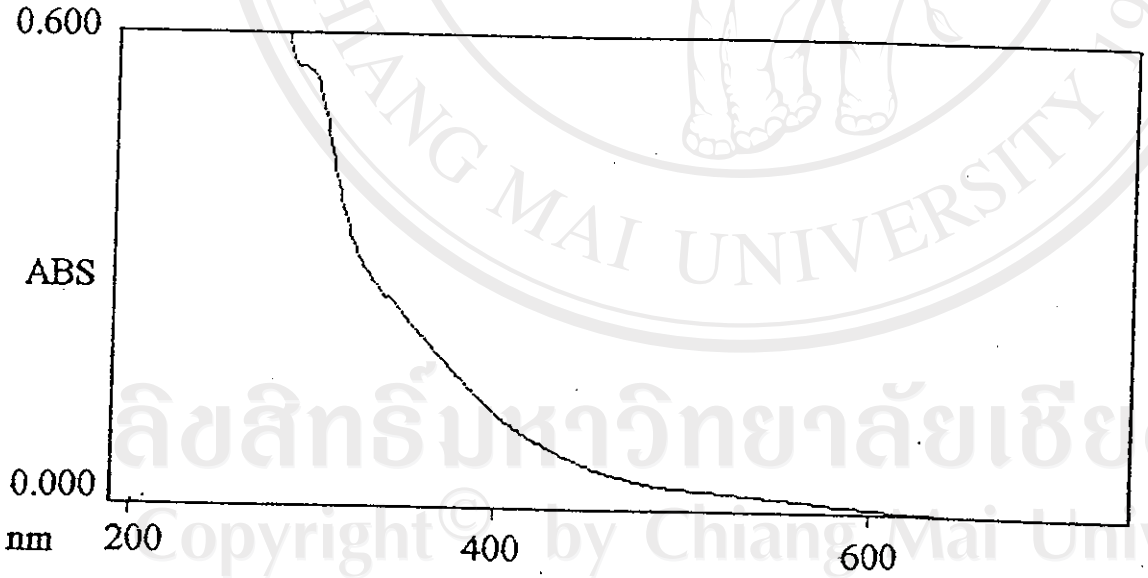

Fig. 3.78 Electronic spectrum of Ni : en -bentonite

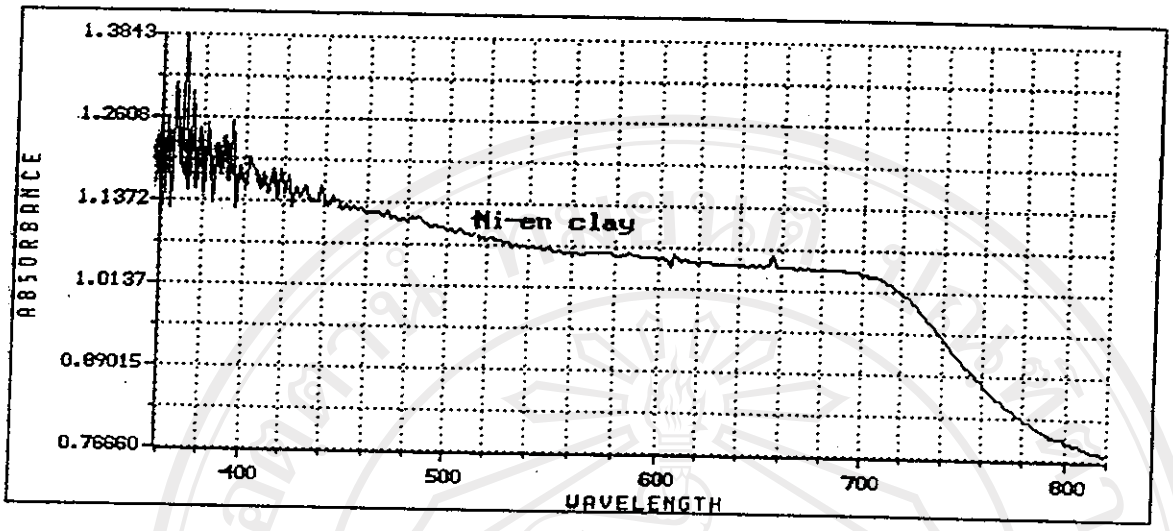

Fig. 3.79 Diffuse reflectance of Ni : en-bentonite