CHAPTER III

Applications of Binuclear Schiff's base Complexes

Since the discovery of salicylidene aniline and its methyl derivatives[1], bidentate and multidentate Schiff's bases have been synthesised[2-6]. They are characterised by the presence of >C=N- bond and are found to be excellent chelating ligands. The coordination chemistry of Schiff's bases as a cyclic polydentate ligands having delocalised orbitals gained importance for over three decades because of their use as models of biological systems[5]. The roles of manganese (II) in its Schiff's bases complexes derived from salicylaldehyde and aliphatic amines are significant in green plant photosynthesis[7].

The light-induced reaction of >C=N- (azomethine group) have been the subject of investigation since last five decades. The large number of known photochemical reactions associated with >C = N - has commonly been treated as a group of separate entities[8].

Schiff's bases are an important class of ligands in coordination chemistry and have many applications in various fields[9-13]. When functional groups such as OH and/or SH with a replaceable hydrogen atom are present sufficiently near to azomethine moiety, formation of stable complexes is facilitated.

In the present investigation successful attempts have been made to correlate the structural changes with fluorescence, pigmentation and biological properties.

Many azomethine pigments are reported in the literature[14-15]. This type of pigments which all have the chromophore >C=N- are best considered into two groups i) as pure organics and ii) metal complexes. Most of the azomethine ligands are yellow or orange and their complexes somewhat brown, green or deep yellow.

Azomethine compounds of hydroxy aldehydes and ketones are reported to be good pigments by Patel & Jejurkar[17]. It is observed that the stereochemical properties of chelated compounds have greater effects on stability and fastness properties of azomethine complexes.

Mixed Schiff's base complexes of transition and nontransition elements as pigments are reported in the literature[18].

Recently the chemistry and biological activity of Schiff's bases and their complexes have created great interest among researchers for the diverse type of biological activities associated with imine moiety[19]. It is also reported that Schiff's bases have a broad spectrum biological activity[20]. The Schiff's bases containing hydroxy, chloro, sulfer, methoxy and heterocyclic rings show good bactericidal character.

Among the Schiff's bases semicarbazones have been found to be useful as anticonvulsants[21], and possess antiphytyriral activity[22]. Thiosemicarbazones and their metal complexes show wide spectrum of medicinal properties. They are active against tuberculosis, leprosy, rheumatism, bacterial and viral infections. They also show antimalarial activity. These activities are often related to complexing abilities of the compounds with metal ions[23-26].

Zinc complexes are proved to be better bactericides than Copper and Nickel complexes[18].

In view of great interest involved in these compounds on account of their immense uses in chemotherapy as well as pigmentation and luminescence, the Schiff's bases and their complexes reported in chapter (II) have been investigated for their (i) Luminescence (ii) Pigmentation and (iii) Bactericidal properties and Applications in this chapter.

3.1 Luminescence Study :

In contrast to incandescence (light emission by thermal sources) luminescence is the emission of optical radiation resulting from non-thermal excitation of the energy levels of atoms, molecules, polymers and crystals.

The luminescent materials have a wide range of applications and can be used for scintillators, luminescent, screens, solid-state LASERS, jewelry, discharge lamps etc.[27].

In this section the organic Schiff's bases and their metal complexes have been studied for their Fluorescence behaviour.

Fluorescence study was carried out using Shimadzo Spectrophotofluorometer RF-500 for hydrazone, m-&p-phenylene-diamine and Benzidine series. In case of Thiocarbohydrazone and Terephthaldehyde series a Perkin Elmer luminescence spectrometer LS-50 using xenon as source with scanning speed of 200mm, Excitation slit 3nm and filter used 350 nm. The Schiff's base ligands and their complexes were studied in three forms :

(1) In powder form at room temperature.

(2) After mechanical deformation by making tablets (under 8 tonn/$(inch)^2$ pressure).

(3) After heat treatment, by heating in oven at 130-150^{o}C for 1 hour and sudden cooling.

The fluorescence spectra were recorded for every series at the same excitation wavelength.

To study the effect of substituents in the ligand and its coordination on fluorescence behaviour the emission spectra were recorded for different excitation wavelengths. The excitation wavelength for which the intensity for emission found out to be maximum, was taken as the excitation wavelength.

i) The fluorescence spectra for m-,p-phenylenediamine and benzidine series was studied at 250 nm. as excitation wavelength.

ii) For hydrazone series at 300 nm excitation wavelength.

iii) Terephthaldehyde series at 200 nm excitation wavelength.

iv) Thiocarbohydrazone series at 200 nm excitation wavelength.

The emission spectra for some representative compounds are shown in graphs (III.1 - III. 21).

3.2 **Pigmentation Study :**

The pigmentation study was done in an emulsion paste.

Formulation of Paste

Acramine Binder SIN	15ml
Kerosene	68ml
Urea	5gm
Ammonium Chloride	2gm

Method :

To 15 ml Acramin binder SIN 68ml kerosene was added slowly with constant high speed stirring for 10 minutes followed by 5 gm Urea and 2 gm Ammonium Chloride. The mixture was stirred with high speed for 10 minutes more.

25gm of the above Paste and 0.5gm Schiff's base complexes were mixed and stirred well for 15 minutes at room

temperature. This was then printed on cotton, Silk and polyster clothes and dried in the oven for one hour at 115-120^{o}C then washed with plenty of water with rubbing, and dried. Rubbing and light fastness were evaluated using standard methods[28,29].

Light fastness

The light fastness was carried out using colour FADE-O-METER type FDA-R No. 8119 using Carbon Arc Lamp.

A description of the method of exposure we have adopted is given below :

The patterns under test were mounted alongside and exposed to light for 8 hours and 12 hours intervals. The Contrasts between each of the exposed and the unexposed pattern were then compared with the corresponding contrasts shown by the faded standards. The light fastness of the pattern was then given as the number of the standard that shows the same contrasts. The contrast between treated and untreated patterns have been assessed by a Grey scale. Qualitative assessment is shown below :

Rating	Quality Assessment
5	Excellent
4	Good
3	Fair
1,2	Poor

The method of assessment using Grey Scales helps materially in presenting a picture of the approximate degree of staining, or the effect on a pattern that is likely to occur when one refers to the fastness figures.

The results of the light fastness assessments are summarised in (Table III.2).

Fastness to Rubbing :

The rubbing fastness (dry and wet) were carried out by SASMIRA CROCKMETER by using International Test[30], details of which are given below :

Test pattern : A piece of dyed material 5 cm x 5 cm

Treatment :(a) dry rubbing test,

The test pattern is rubbed with a piece of dry white cotton lawn.

(b) Wet rubbing test,

The test pattern is rubbed with a piece of white cotton Lawn previously wetted.

The tests are carried out with a Crockmeter, 10 to-and-fro movements in 10 seconds being made for each test.

The test cloth from the wet test is dried in air at room temperature.

The degree of staining of the two test clothes have been assessed by using Grey Scale.

Qualitative assessment is shown below :

Observation	Grade	Qualitative assessment
No dye stain	5	Excellent
Slight dye stain	4	Very good
Moderate dye stain	3	Good
Distinct dye stain	2	Fair
Very much Distinct dye stain	1	Poor

The results of assessments are given in Table (III.2)

3.3 **Antibacterial Study** :

The bactericidal activity of Schiff's bases has been studied in the early days of chemotherapy. The Schiff's base complexes of different metals also show antibactericidal activity. The potential of metal chelates as drug is now well established[19,20,23-26].

In this work some of the selected compounds which are soluble were tested for thier antibacterial activity by cup-plate method[31], in DMF solvent against Escherichia Coli (gram negative) as test organism, using nutrient agar as medium.

The compounds were used at concentration of 10mg/ml in DMF.

The detailed procedure is given below :

Antibacterial test :

Sterile nutrient agar plates containing 30ml nutrient agar, and sterile nutrient broth tubes containing 5 ml nutrient broth were prepared under sterile conditions.

E.Coli was grown for 4-5 hours in nutrient broth under submerged condition. The exponential phase cells were plated on nutrient agar plates under sterile conditions, and 1 cm wide wells were bored using a sterile borer. Solution containing 0.1mg/ml of the compounds were prepared in Dimethylformamide and 0.1 ml of this sample was transferred to plates. The plates were kept at about $20^{o}C$ for the diffusion of the compounds. The plates were then carefully kept at $37^{o}C$ for 12 hours. The zone of inhibition was checked around the wells.

TABLE III. 1

Evaluation of Fastness Properties of Schiff's base complexes as pigments

Ser No.	Compound	Light Fastness			Rubbing Fastness					
					Dry			Wet		
		Cotton	Polyester	Silk	Cott-on	Polye-ster	Silk	Cott-on	Polye-ster	Silk
1-	BHBH	4	4-5	5	3-4	4	4	3	3-4	3-4
2-	BHBH-Cu(II)	5	5	5	4	4-5	5	4	4-5	5
3-	BHBH-Ni(II)	5	5	5	4	4-5	5	4	4-5	5
4-	BHBH-Zn(II)	5	5	5	4	4-5	4	4	4-5	5
5-	BDBH	4-5	4-5	5	3-4	4	4	3	3	4
6-	BDBH-Cu(II)	5	5	5	4	5	5	4	5	5
7-	BDBH-Ni(II)	5	5	5	4	5	5	4	5	5
8-	BDBH-Zn(II)	5	5	5	4	4-5	5	4	4	5
9-	BHMBH	4	5	5	4	4	4	3	3	3-4
10-	BHMBH-Cu(II)	5	5	5	5	5	5	5	5	5
11-	BHMBH-Ni(II)	5	5	5	5	5	5	5	5	5
12-	BHMBH-Zn(II)	5	5	5	4	5	5	4	4	5
13-	BHNH	4	4	5	4	4	4	3	3	3
14-	BHNH-Cu(II)	5	5	5	4	5	5	4	4	5
15-	BHNH-Ni(II)	5	5	5	4	5	5	4	4	5
16-	BHNH-Zn(II)	5	5	5	5	5	5	4	4	5
17-	BHBT	4	5	5	4	4	5	3	2-3	3
18-	BHBT-Cu(II)	5	5	5	5	5	5	4	5	5
19-	BHBT-Ni(II)	5	5	5	5	5	5	4	5	5
20-	BDBT	4	5	5	4	4	5	3	3	4
21-	BDBT-Ni(II)	5	5	5	5	5	5	4	4	5
22-	BDBT-Zn(II)	5	5	5	5	5	5	4	4	5

23-	BHMBT	5	5	5	4	4	5	3	3	4
24-	BHMBT-Cu(II)	5	5	5	5	5	5	4	4-5	5
25-	BHMBT-Ni(II)	5	5	5	5	5	5	4	4-5	5
26-	BHNT	4	5	5	4	4	4	3	3	4
27-	BHNT-Zn(II)	5	5	5	4	5	5	4	4	5
28-	BDB-P-PD	5	5	5	4	4	4	3-4	4	4
29-	BDB-Cu(II)	5	5	5	5	5	5	5	5	5
30-	BDB-Ni(II)	5	5	5	5	5	5	5	5	5
31-	BHMB-p-PD	5	5	5	4	4	4	3-4	4	4
32-	BHMB-p-PD-Cu(II)	5	5	5	5	5	5	4	4	5
33-	BHMB-p-PD-Ni(II)	5	5	5	5	5	5	4	5	5
34-	BHN-p-PD	5	5	5	5	4	4	3	4	4
35-	BHN-p-PD-Ni(II)	5	5	5	5	4	4	3-4	5	5
36-	BHN-p-PD-Zn(II)	5	5	5	4	4	4	4	4	5
37-	BDB-m-PD	5	5	5	5	4	4	3	4	4
38-	BDB-m-PD-Cu(II)	5	5	5	5	5	5	4	4	5
39-	BDB-m-PD-Ni(II)	5	5	5	5	5	5	4	4	5
40-	BHMB-m-PD	5	5	5	5	4	4	3-4	4	4
41-	BHMB-m-PD-Cu(II)	5	5	5	5	5	5	4	5	5
42-	BHMB-m-PD-Zn(II)	5	5	5	5	5	5	5	5	5
43-	BHBB	5	5	5	5	4	4	3-4	4	4
44-	BHBB-Cu(II)	5	5	5	5	5	5	4	5	5
45-	BHBB-Ni(II)	5	5	5	5	5	5	4	5	5
46-	BHBB-Zn(II)	5	5	5	5	5	5	4	5	5
47-	BDBB	5	5	5	4	4	5	4	4	5
48-	BDBB-Cu(II)	5	5	5	5	5	5	4	5	5
49-	BDBB-Ni(II)	5	5	5	5	5	5	4	5	5
50-	BDBB-Zn(II)	5	5	5	5	5	5	4	5	5

51-	BHMBB	5	5	5	4	4	4	4	4	5
52-	BHMBB-Cu(II)	5	5	5	5	5	5	4	4	5
53-	BHMBB-Ni(II)	5	5	5	5	5	5	4	5	5
54-	TBIG	5	5	5	5	4	5	4	4	5
55-	TBIG-Cu(II)	5	5	5	5	4	5	4	4	4
56-	TBIG-Ni(II)	5	5	5	5	5	5	4	4	4
57-	TBIA-Cu(II)	5	5	5	4	4	4	3-4	4	5
58-	TBIA-Ni(II)	5	5	5	5	4	5	4	4	5
59-	TBIH-Cu(II)	5	5	5	5	5	5	4	5	5

5 = (excellent), 4 = (good), 3 = (Fair), 1,2 = (Poor)

TABLE (III. 2)

Antibacterial Activity of the soluble compounds

Ser. No.	Compound	E.Coli
1-	BHBH	-
2-	BHBH-Cu(II)	+
3-	BHBH-Ni(II)	++
4-	BHBH-Zn(II)	+
5-	BDBH	-
6-	BDBH-Cu(II)	+
7-	BDBH-Ni(II)	++
8-	BDBH-Zn(II)	+
9-	BHMBH	+
10-	BHMBH-Cu(II)	++
11-	BHMBH-Ni(II)	++
12-	BHMBH-Zn(II)	++
13-	BHNH	-
14-	BHNH-Cu(II)	+
15-	BHNH-Ni(II)	+
16-	BHNH-Zn(II)	+
17-	BHBT	+
18-	BHBT-Cu(II)	+
19-	BHBT-Ni(II)	++
20-	BHBT-Zn(II)	+
21-	BDBT	+
22-	BDBT-Cu(II)	+
23-	BDBT-Ni(II)	++

24-	BDBT-Zn(II)	+
25-	BHMBT	+
26-	BHMBT-Cu(II)	++
27-	BHMBT-Ni(II)	+++
28-	BHMBT-Zn(II)	+
29-	BHNT	+
30-	BHNT-Cu(II)	+
31-	BHNT-Ni(II)	++
32-	BHNT-Zn(II)	+
33-	BHB-m-PD	-
34-	BHB-m-PD-Cu(II)	+
35-	BHB-m-PD-Ni(II)	++
36-	BHB-m-PD-Zn(II)	+
37-	BDB-m-PD	-
38-	BDB-m-PD-Cu(II)	++
39-	BDB-m-PD-Ni(II)	++
40-	BDB-m-PD-Zn(II)	+
41-	BHMB-m-PD	+
42-	BHMB-m-PD-Cu(II)	++
43-	BHMB-m-PD-Ni(II)	+++
44-	BHMB-m-PD-Zn(II)	+
45-	BHN-m-PD	-
46-	BHN-m-PD-Cu(II)	+
47-	BHN-m-PD-Ni(II)	++
48-	BHN-m-PD-Zn(II)	+

Activity : (+++) = high, (++) = moderate
(+) = slight (-) = inactive

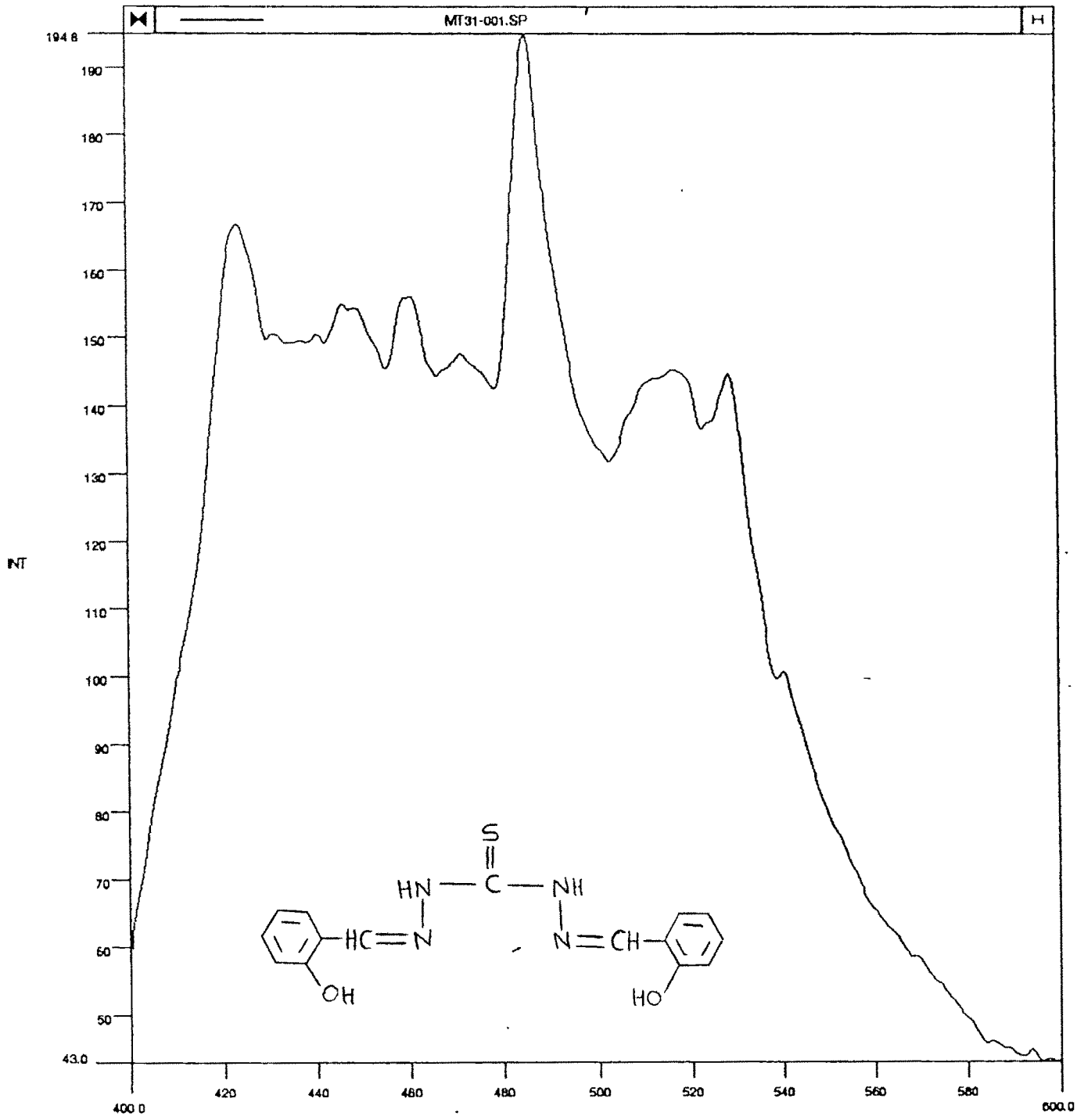

Fig.(III.1) : Fluorescence spectra of BHBT

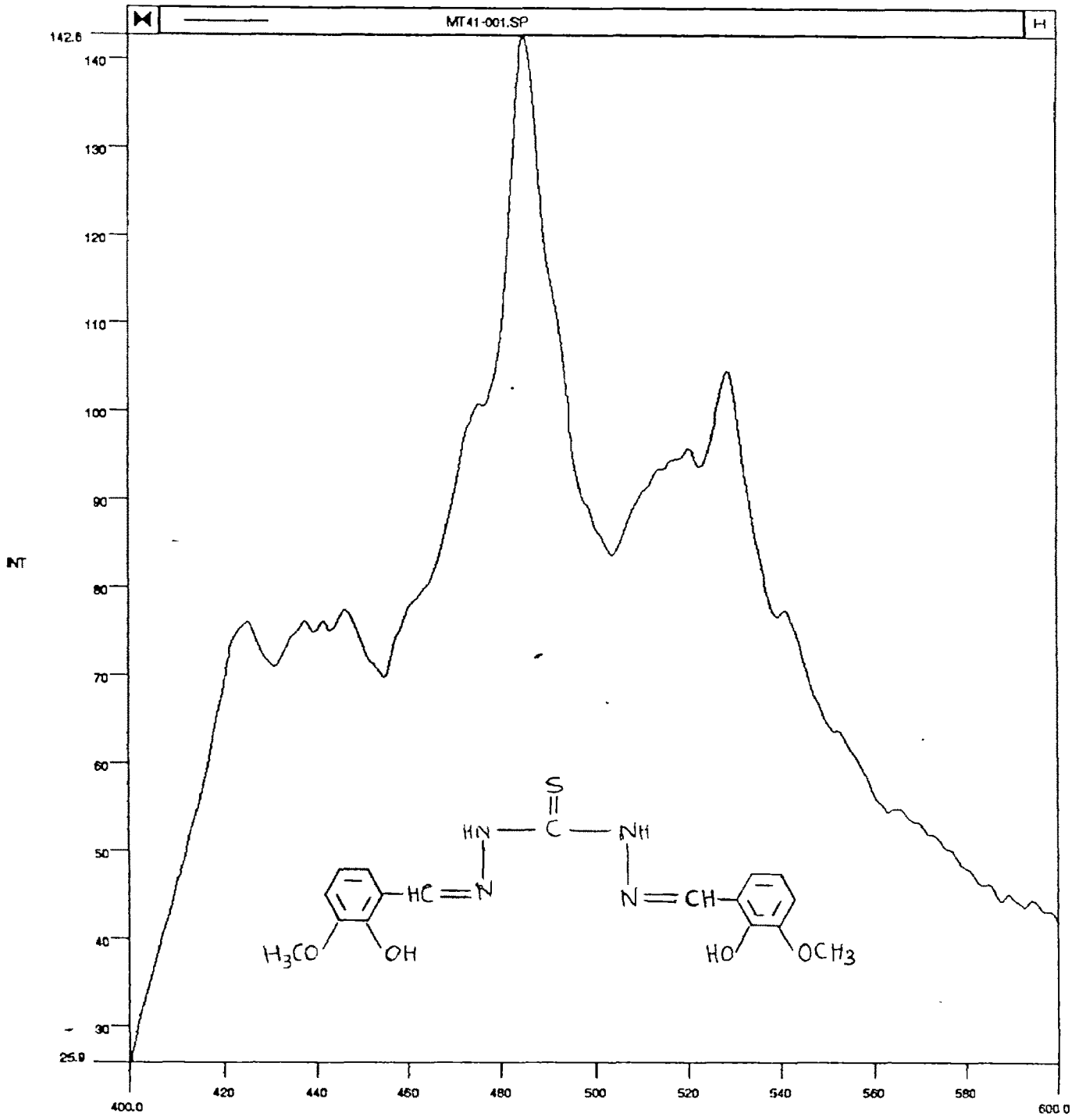

Fig.(III.2) : Fluorescence spectra of BHMBT

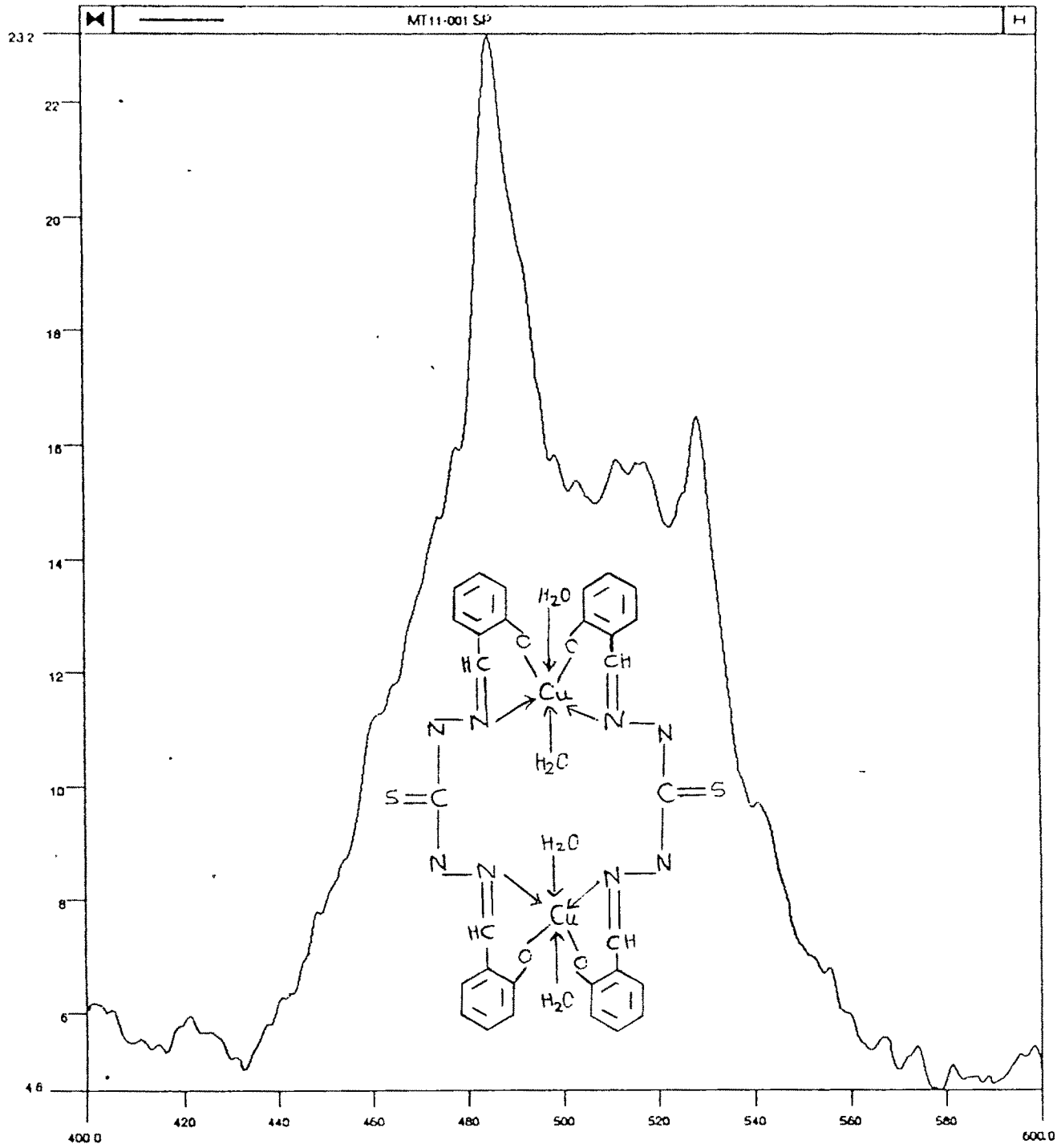

Fig.(III.3) : Fluorescence spectra of BHBT-Cu(II)

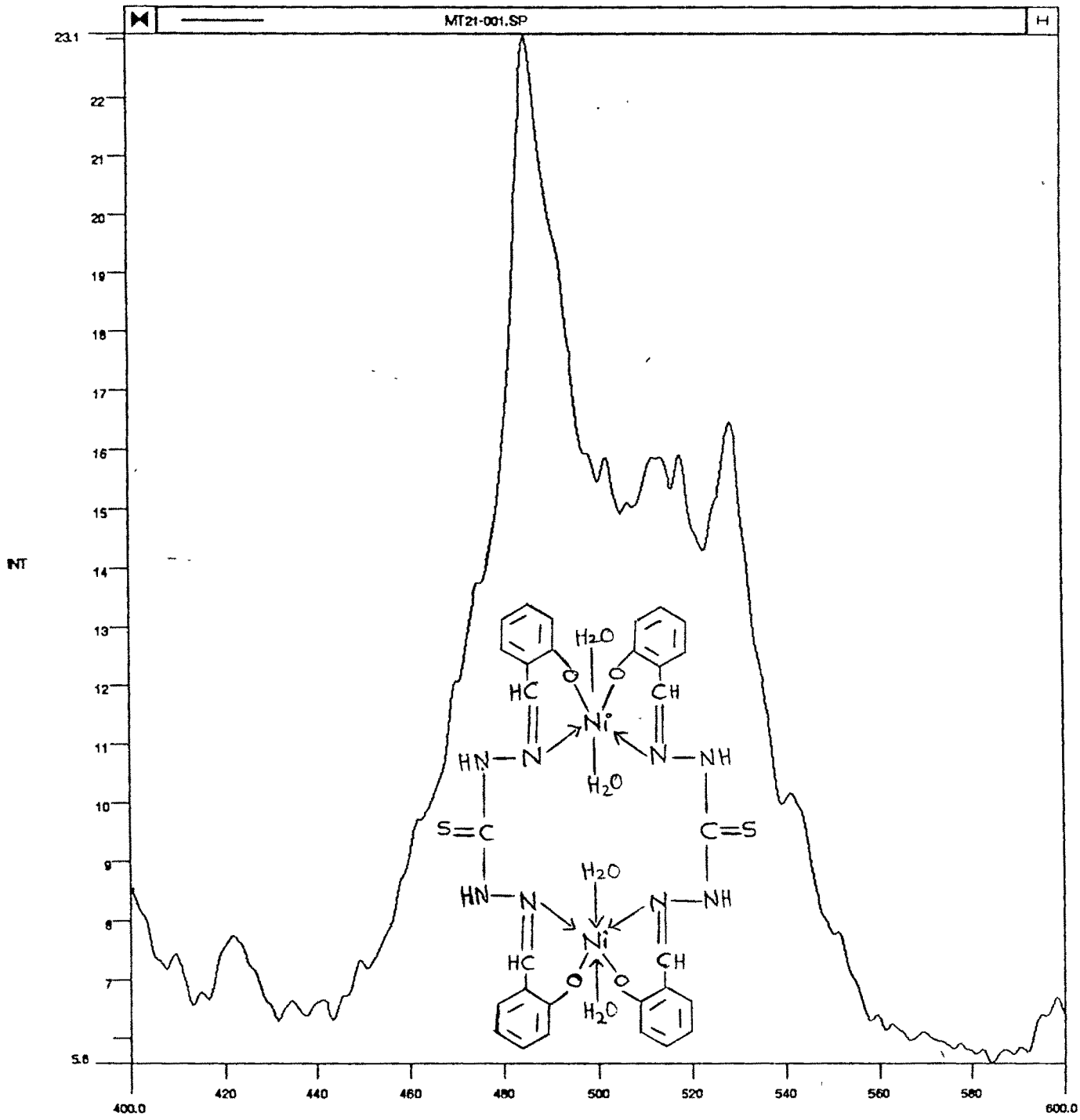

Fig.(III.4) : Fluorescence spectra of BHBT-Ni(II)

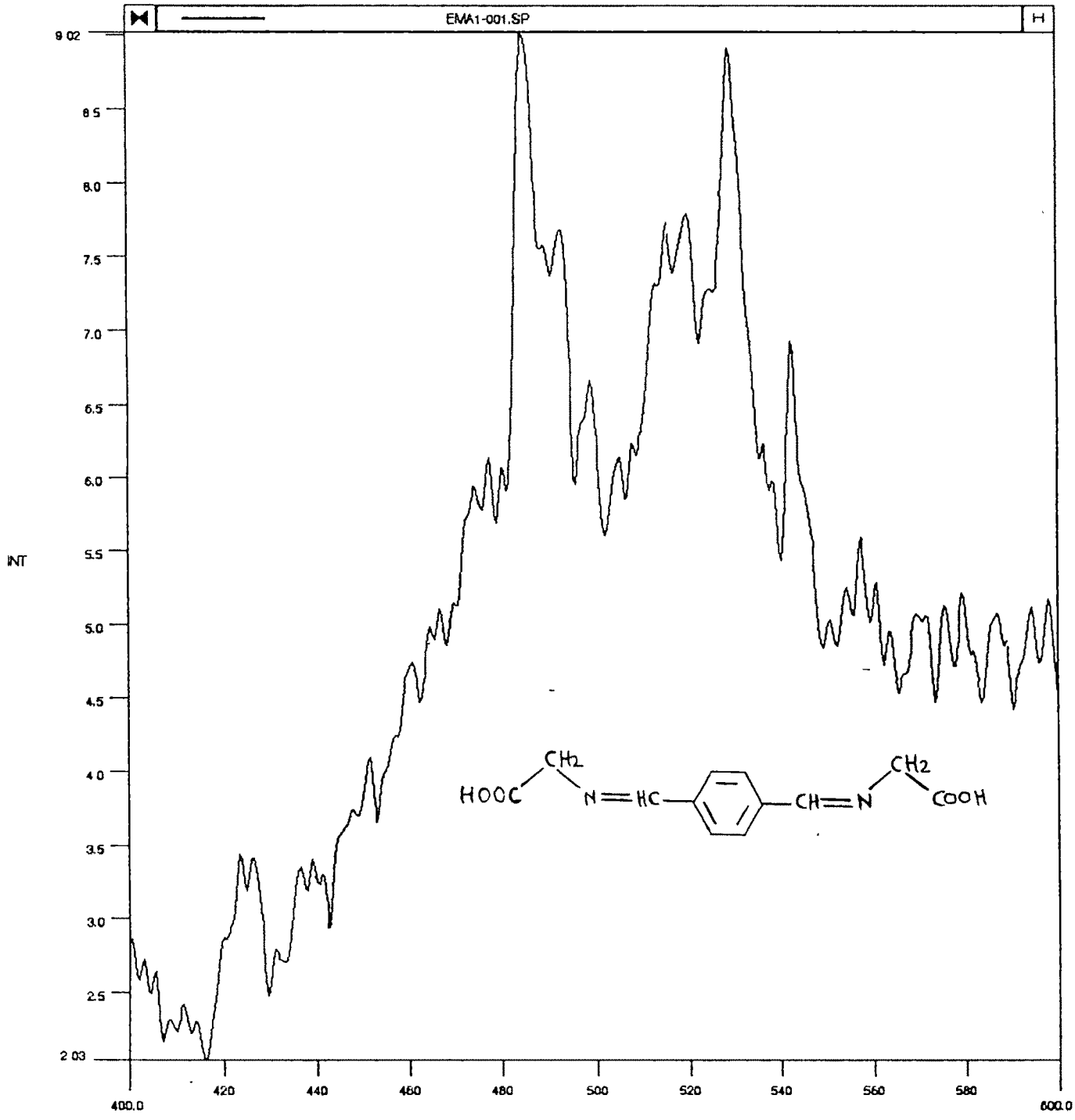

Fig.(III.5) : Fluorescence spectra of TBIG

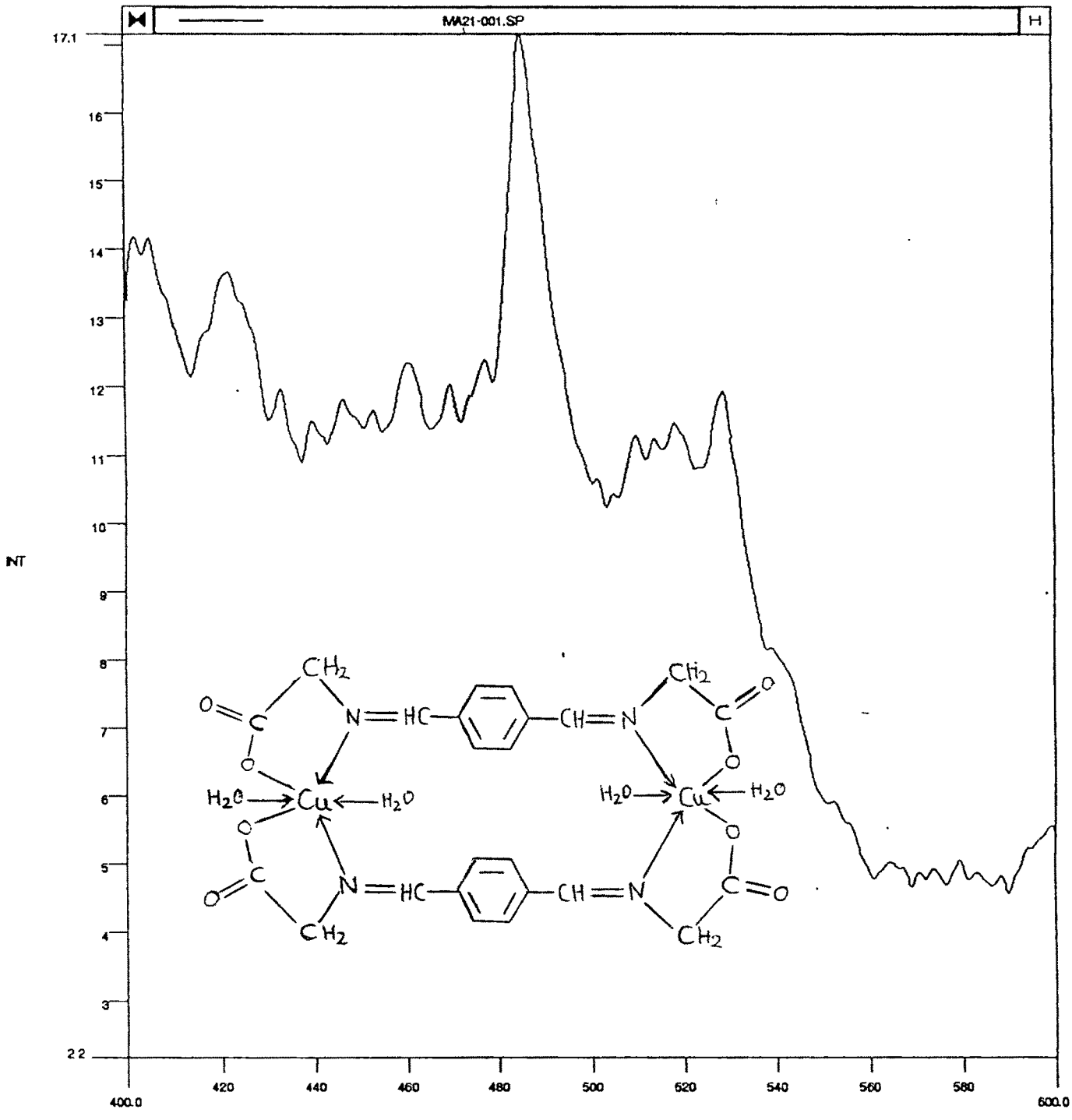

Fig.(III.6) : Fluorescence spectra of TBIG-Cu(II)

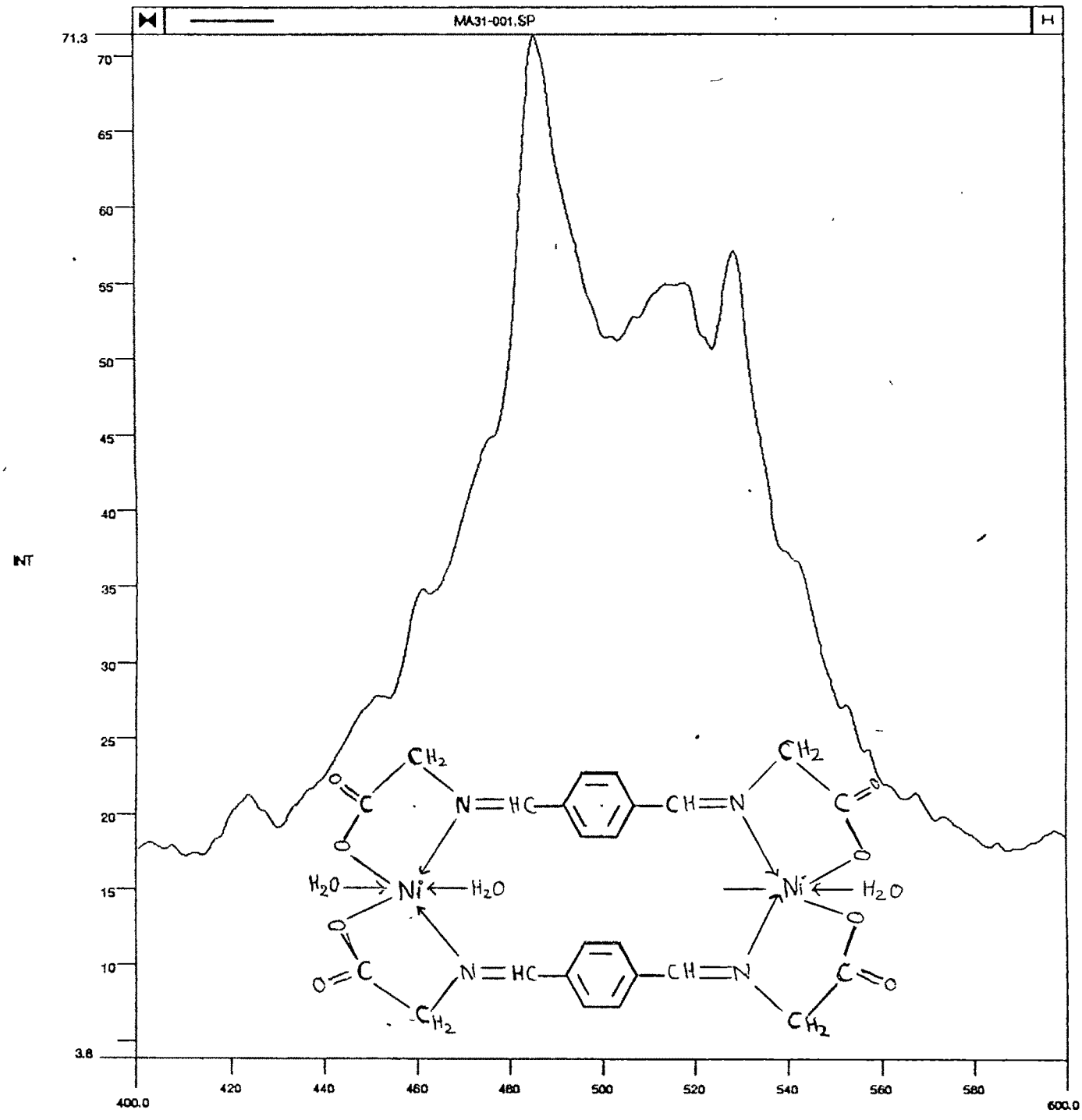

Fig.(III.7) : Fluorescence spectra of TBIG-Ni(II)

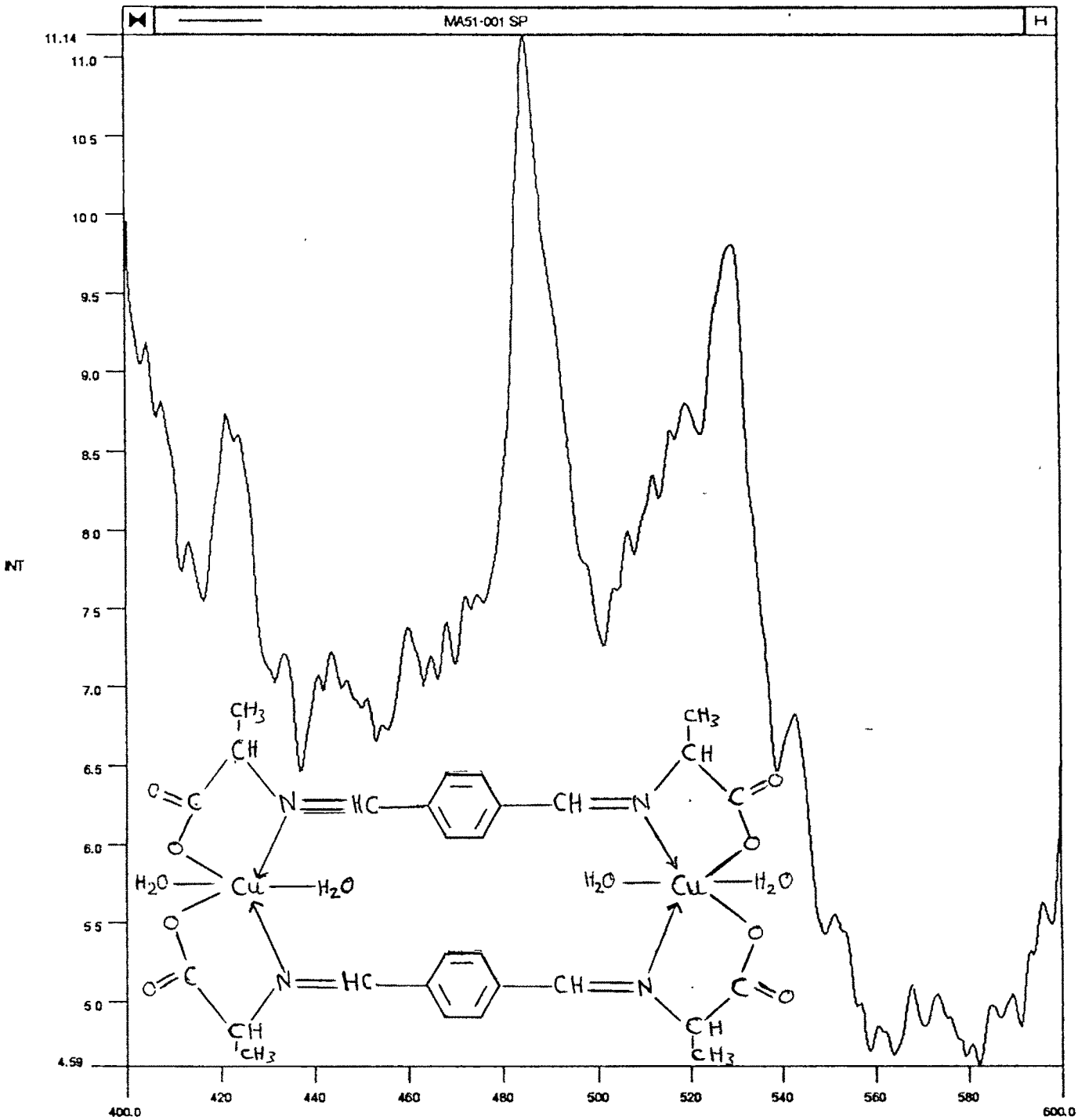

Fig.(III.8) : Fluorescence spectra of TBIA-Cu(II)

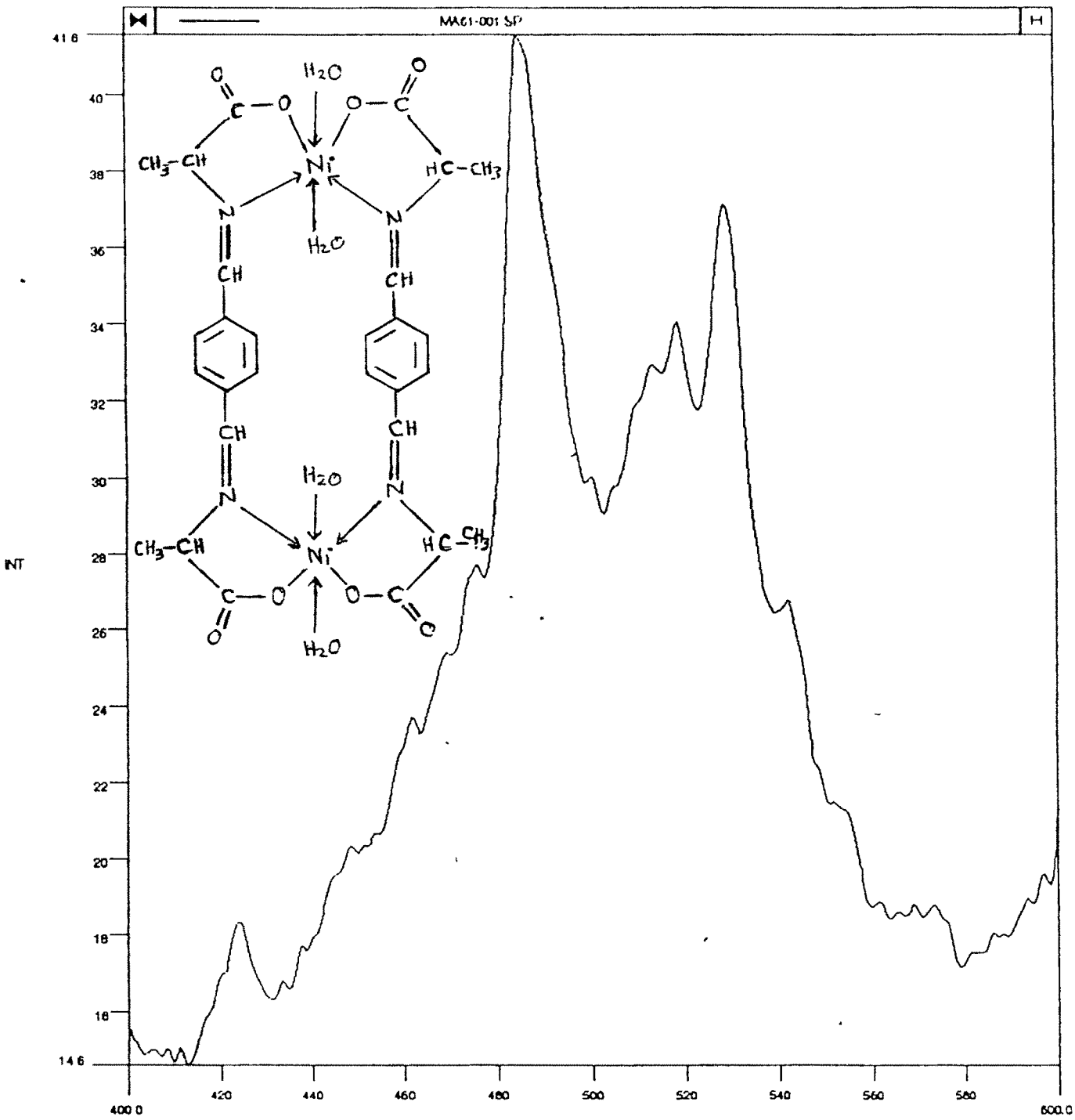

Fig.(III.9) : Fluorescence spectra of TBIA-Ni(II)

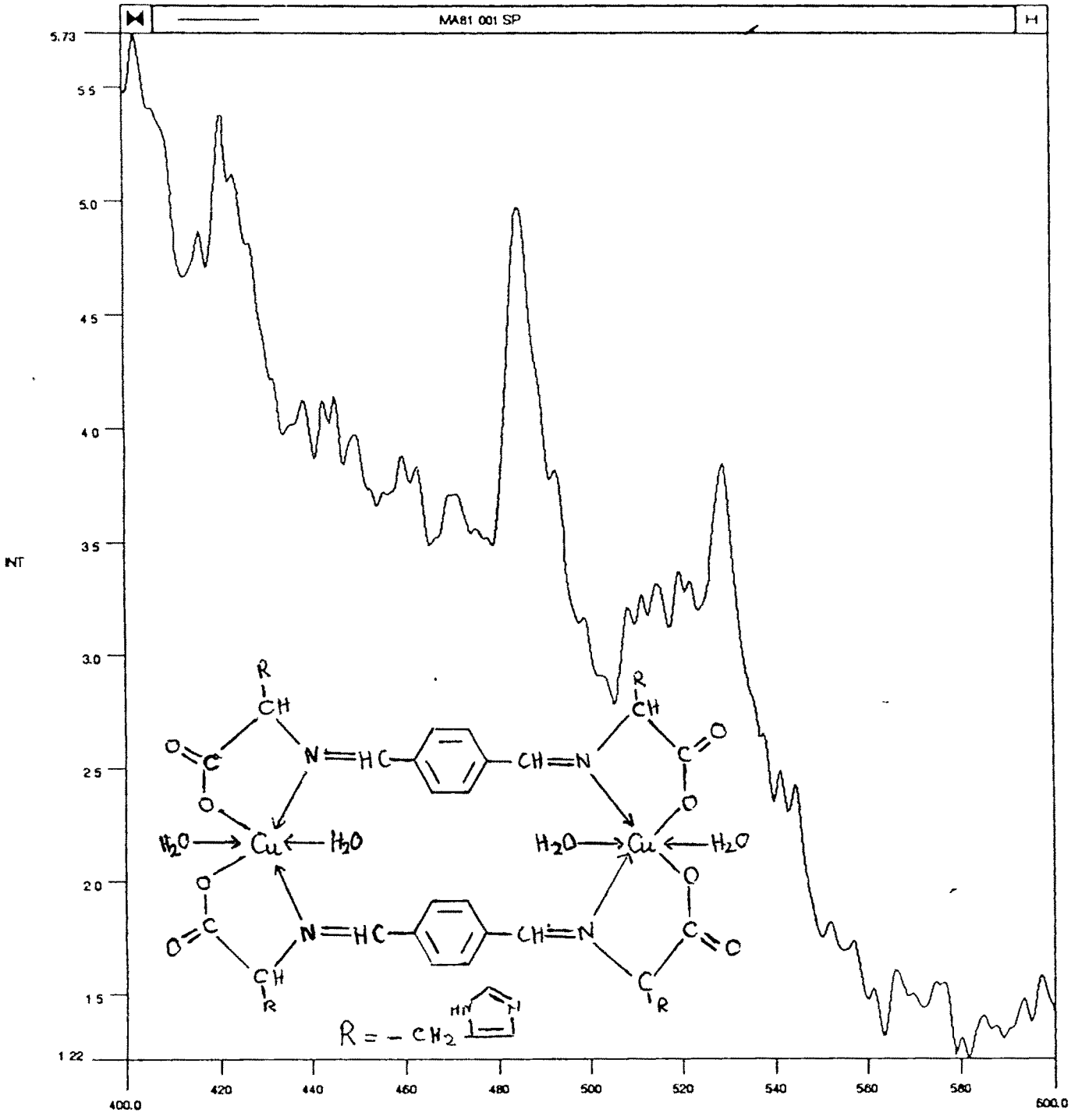

Fig.(III.10): Fluorescence spectra of TBIH-Cu(II)

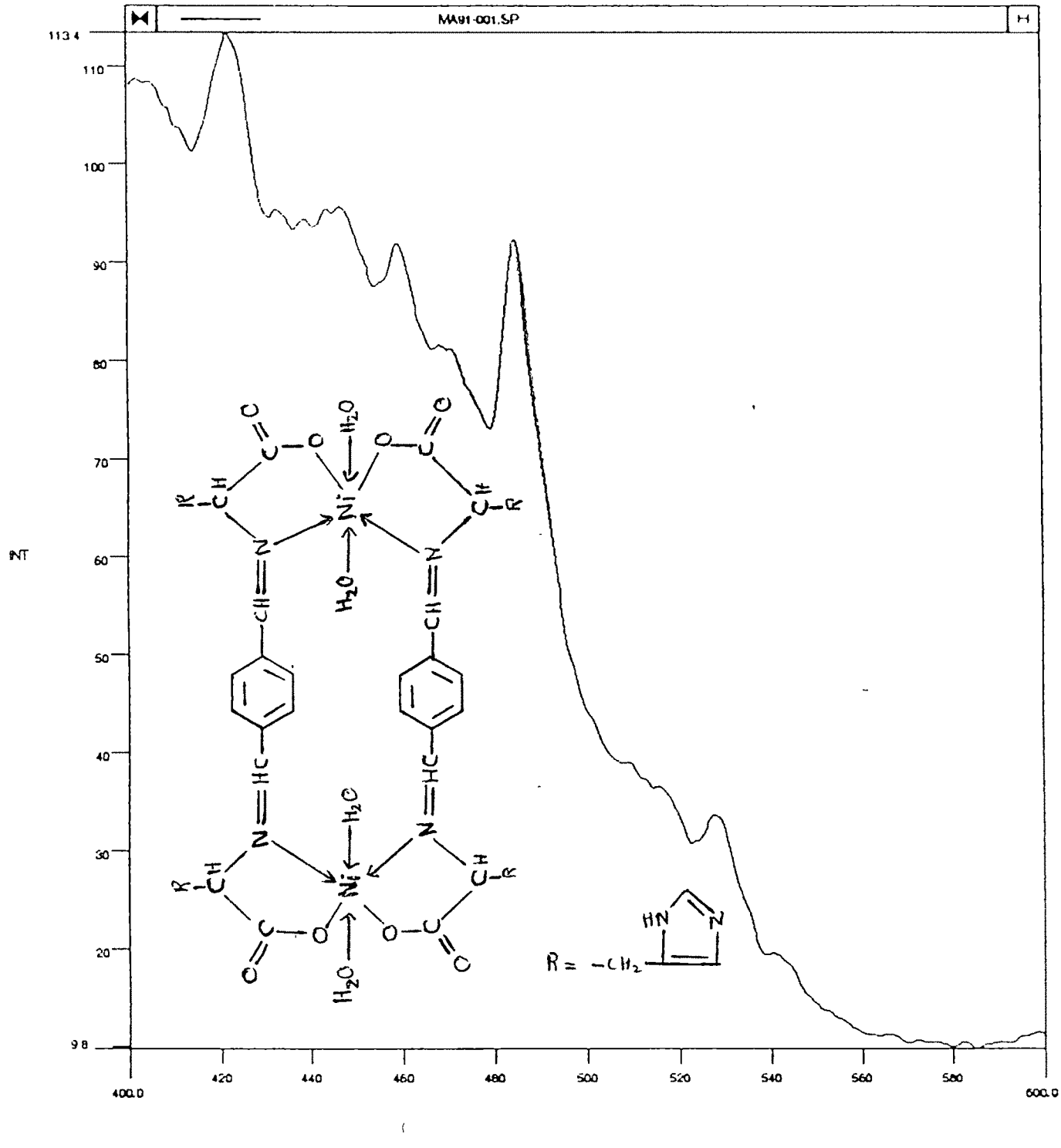

Fig.(III.11): Fluorescence spectra of TBIH-Ni(II)

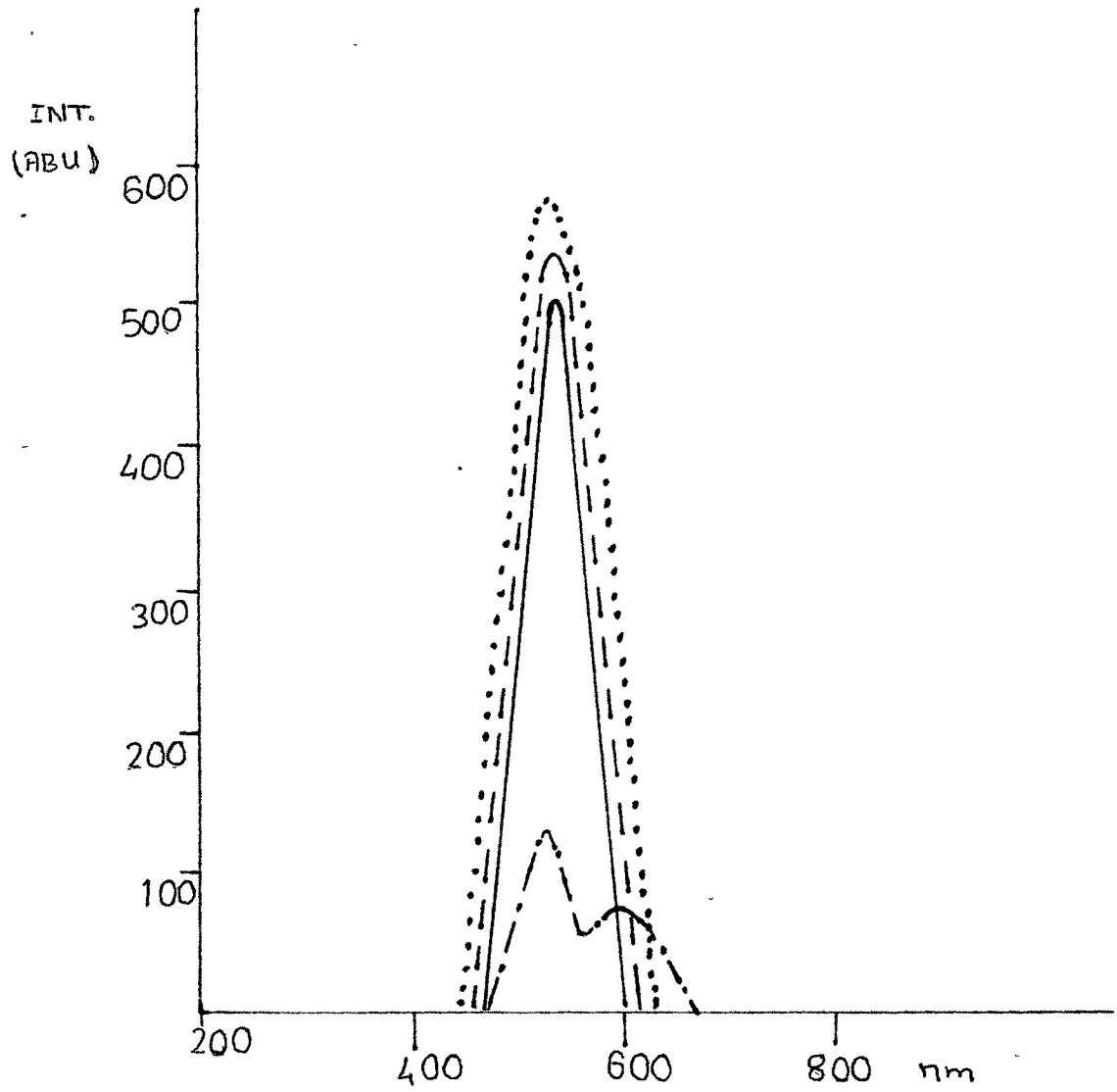

Fig.(III.12): Fluorescence spectra of

(i) BHBH (——),
(ii) BHBH - Cu(II) (----)
(iii) BHBH - Ni(II) (....)
(iv) BHBH - Zn(II) (-.-.-.)

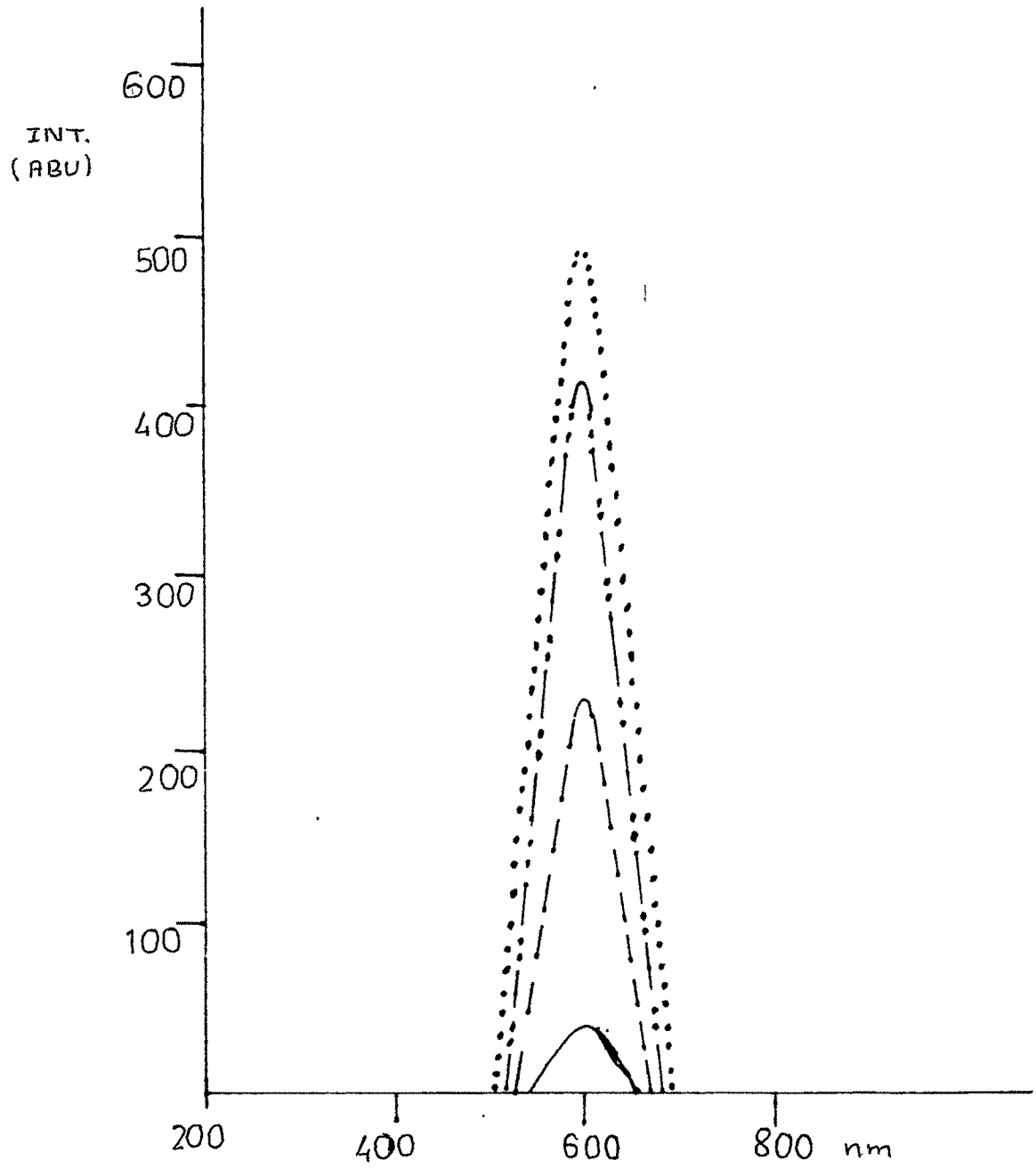

Fig.(III.13): Fluorescence spectra of

(i) BHMBH (----)
(ii) BHMBH - Cn(II) (....)
(iii) BHMBH - Ni(II) (-..-..)
(iv) BHNH (----)

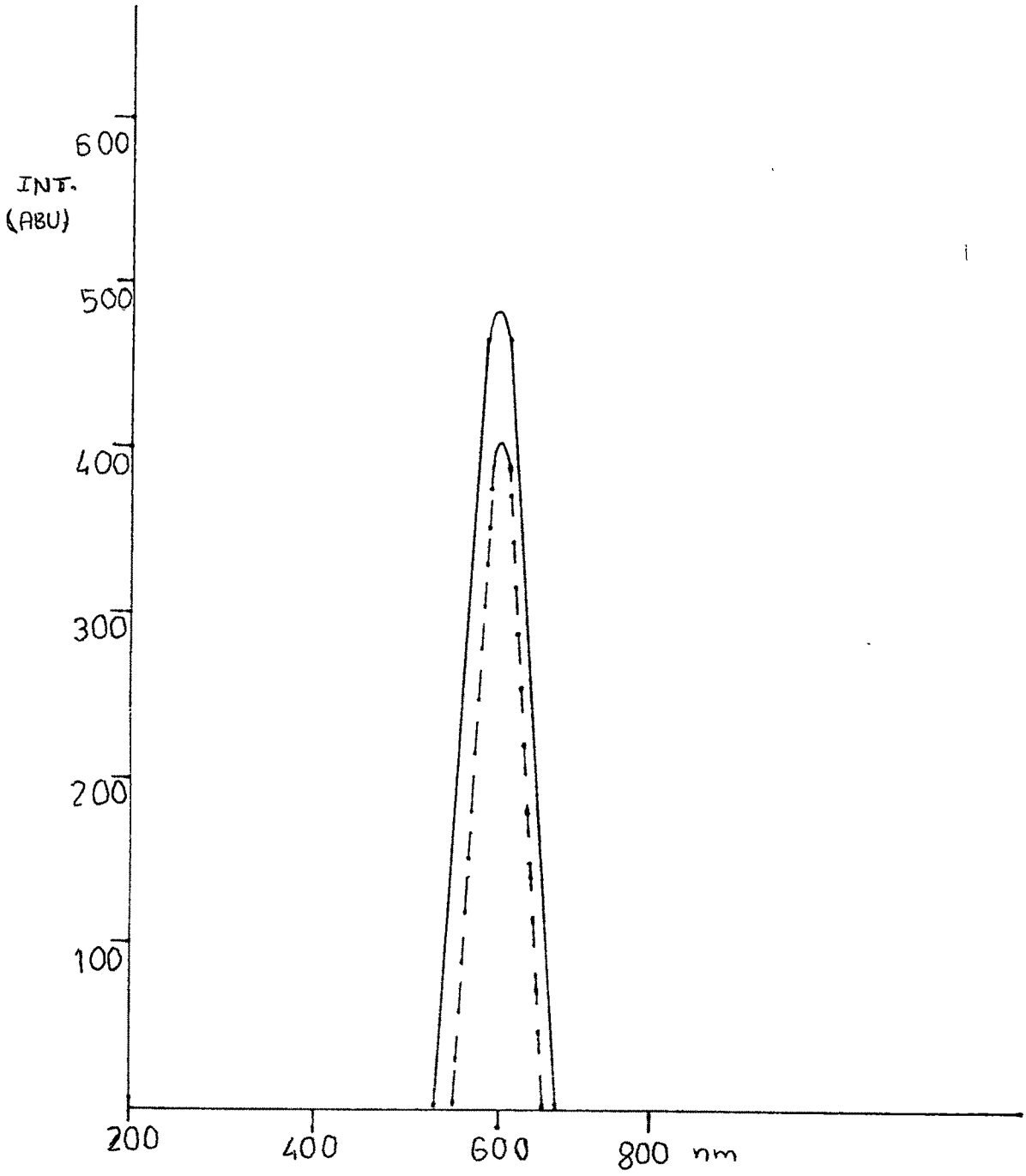

Fig.(III.14): Fluorescence spectra of some mechanically treated specimens

(i) BHBH (——)
(ii) BHMBH (----)

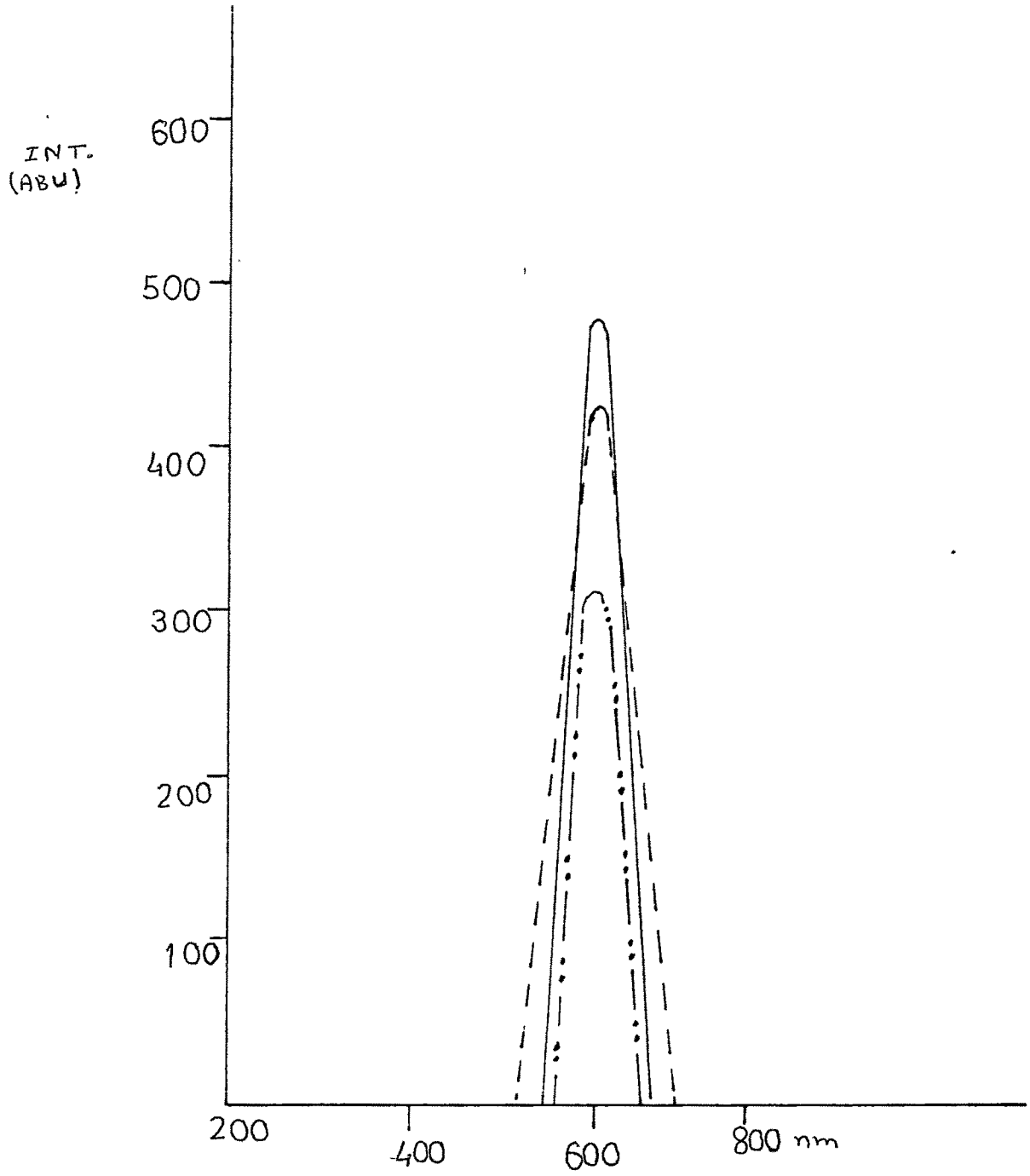

Fig.(III.15): Fluorescence spectra of some mechanically treated specimens

(i) BHBH - Cu(II) (----)
(ii) BHBH - Ni(II) (——)
(iii) BHBH - Zn(-..-..-)

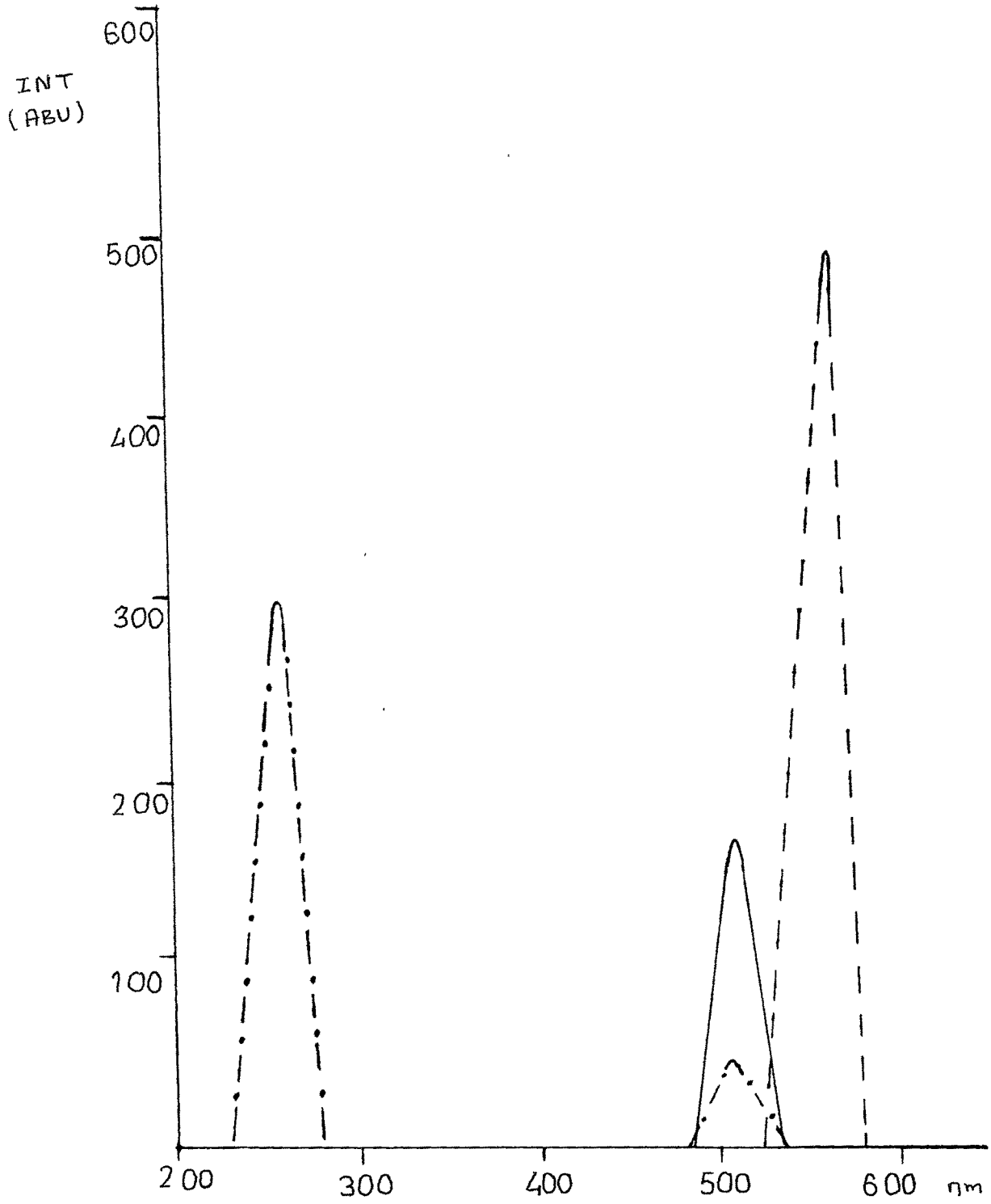

Fig.(III.16): Fluorescence spectra of

(i) BHBB (——),
(ii) BHMBB (----)
(iii) BHNB (-.-.-.)

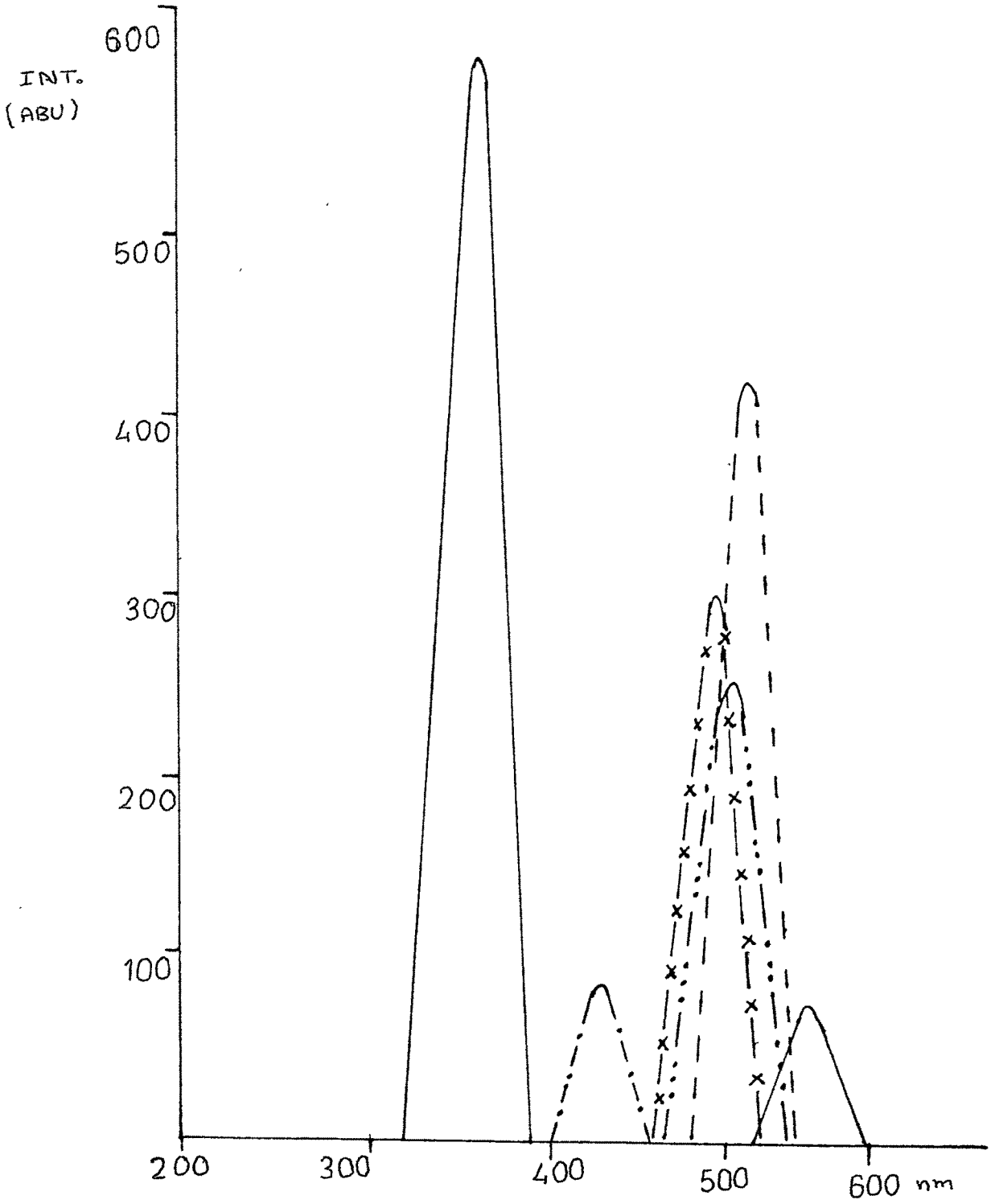

Fig.(III.17): Fluorescence spectra of

(i) BHB-P-PD (——),
(ii) BHMB-P-PD (----)
(iii) BHN-P-PD (-.-.-.),
(iv) BHB-M-PD (-...-...-)
(v) BHMB-M-PD (-x-x-x)

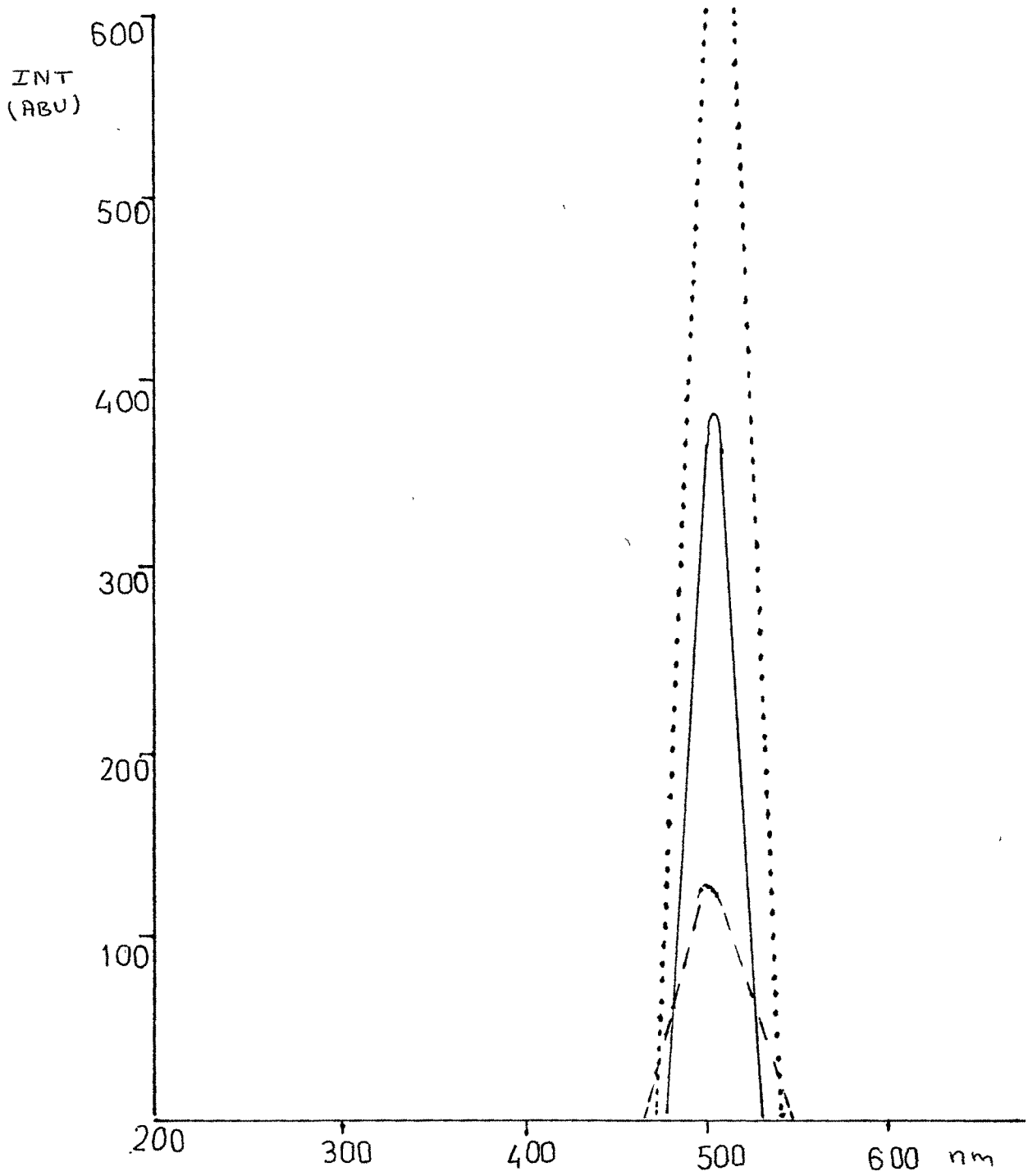

Fig.(III.18): Fluorescence spectra of

(i) BHMB-P-PD-Ni(II) (.....)
(ii) BHMB-P-PD-Zn(II) (----)
(iii) BHMB-P-PD-Cu(II) (——)

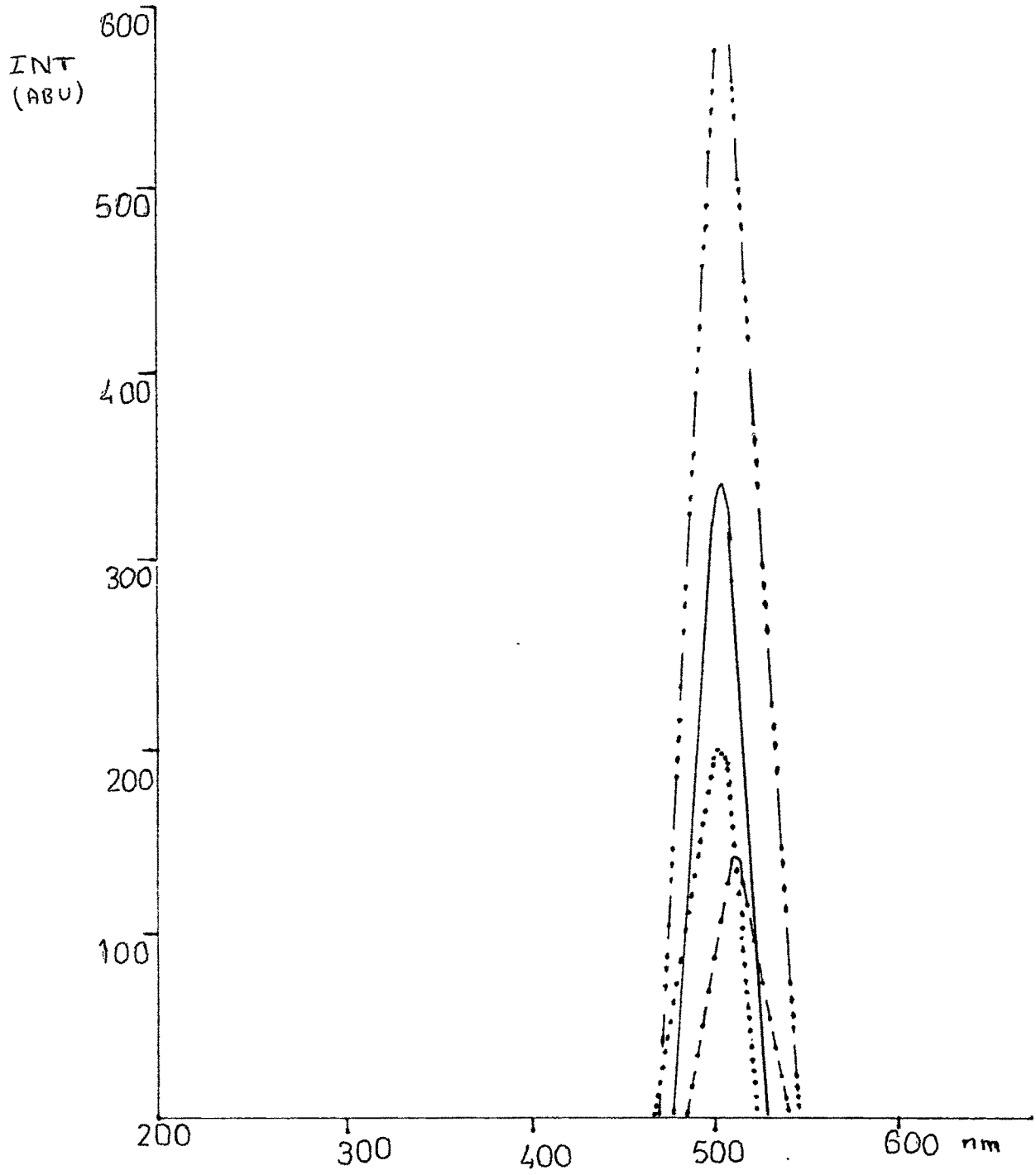

Fig.(III.19): Fluorescence spectra of

(i) BHBB-Cu(II) (----)
(ii) BHMB-Cu(II) (——)
(iii) BHNB-Cu(II) (....)
(iv) BHB-m-PD-Ni(II) (--...--)

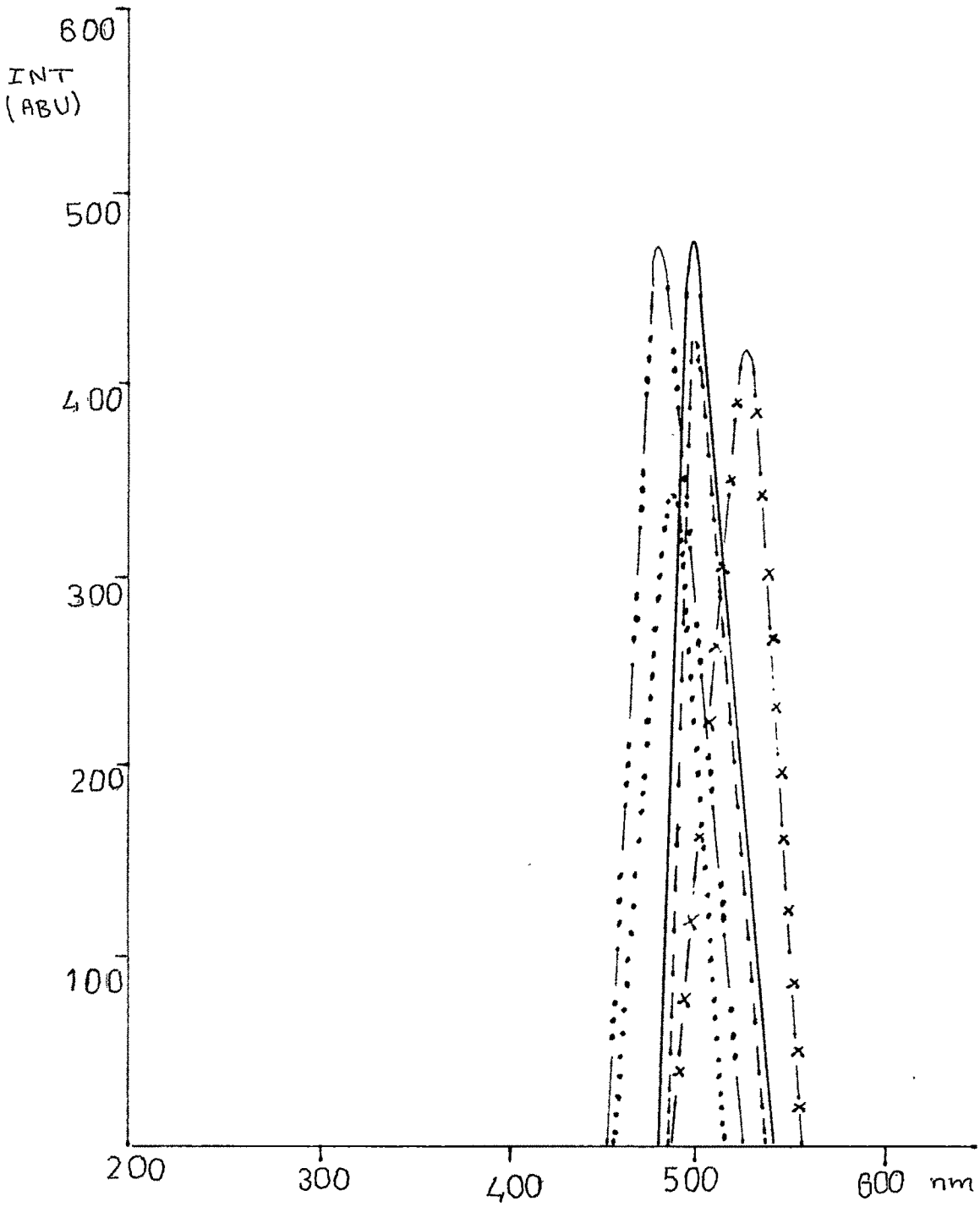

Fig.(III.20): Fluorescence spectra of some mechanically treated specimens.

(i) BHMBB (----)
(ii) BHMBB-Cu(II) (....)
(iii) BHMBB-P-PD (——)
(iv) BHBB-Cu(II) (--...--)
(v) BHB-M-PD-Ni(II) (-x-x-)

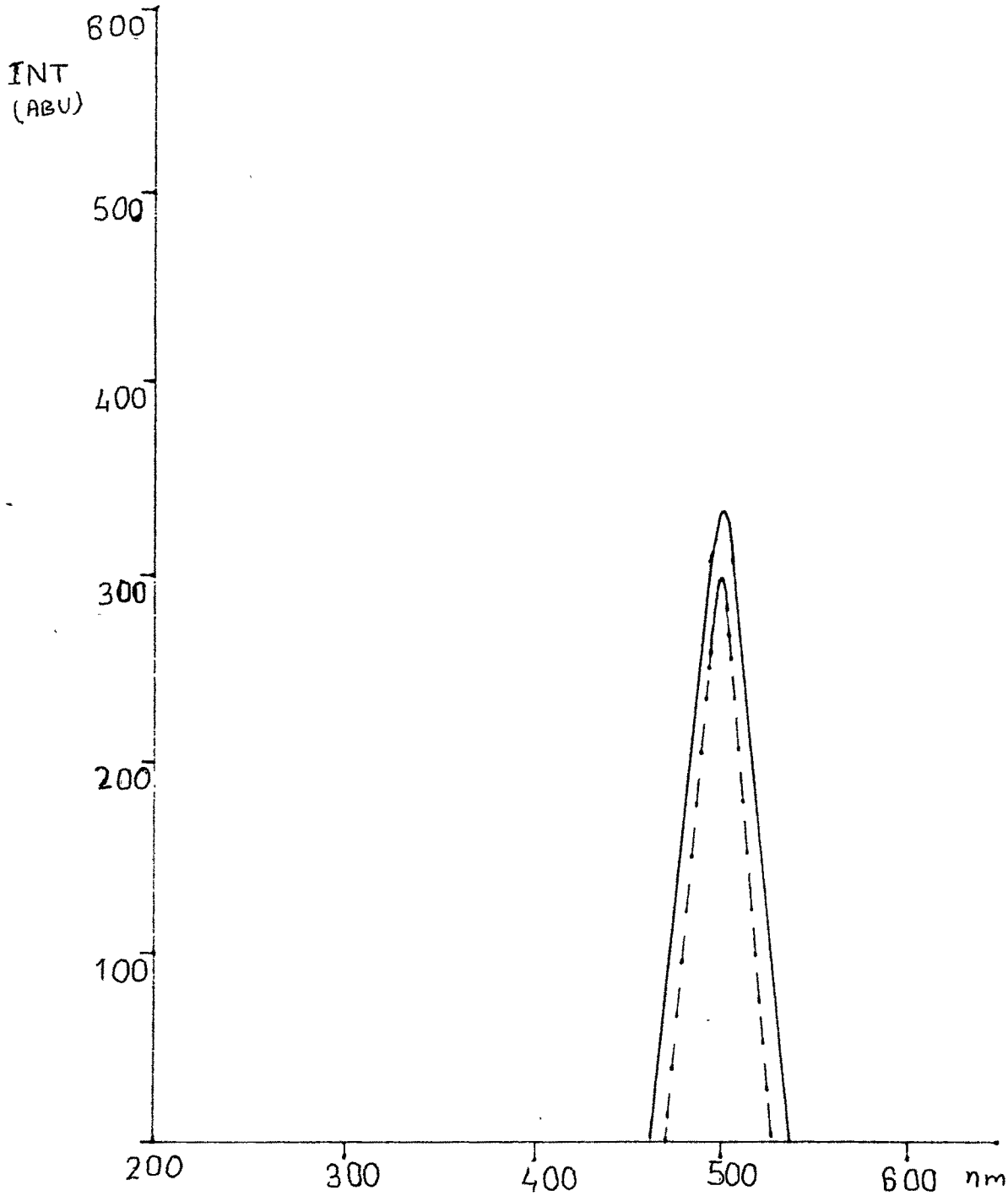

Fig.(III.21): Fluorescence spectra of some thermally treated specimens

(i) BHMBB (——)
(ii) BHMBB-Cu(II) (----)

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