Results and discussion

Chapter III

Instrumental techniques and structural aspects of dyes and its complexes

The instrumental techniques and characterization of dyes and its complexes are described in this chapter. Characterization of the dyes and its complexes were carried out by elemental analysis, infrared spectroscopy (IR), ultraviolet spectroscopy (UV) and EPR spectroscopy .

Elemental analysis of dyes and metal complexes are shown in (Table .3.1.1-3.1.4) all cases1:2 (M: L) solid complexes are isolated and found to have the general formula [ML_2]. The solubility of the complexes in DMSO and DMF. Dyes (Fig.2.1) are a bidentate ligand with nitrogen, azo nitrogen and hydroxyl oxygen as the coordination sites which usually forms 1:2 metal: ligand, chelates (Fig .2.1). All the complexes and the ligand are coloured, soluble in DMSO and DMF.

Fourier transforms infrared (FTIR) spectroscopy

The FTIR spectra of the dyes and metallo dyes were recorded in the 400-4000cm^{-1} range on a Perkin Elmer FTIR on KBr disc.FTIR spectra of dyes and metallo dyes were recorded using KBR pellet (Table 3.2.1-3.2.4).IR spectra of the ligand show a broad at 3936 cm^{-1}due to the OH groups (Fig.3.1-3.4). In the metal complexes, this broad band is still broad due to other groups. The stretching vibration of the phenothiazine γ (C=N) is observed in the form of an intense band at 1576 cm^{-1} in the free ligand. The involvement of the deprotonated γ (C-N) napthalein-1-ol (Remazol red B), cyclopentanol (Golden yellow HER) and disodium napthanol (Amaranth) shows band at 1203 cm^{-1},1198 $cm^{-1}$and 1171 cm^{-1} respectively .

The spectra region at 1650 cm^{-1} is complicated because of the stretching modes of –C=C and –N=N- which are superimposed in the same region. However, the band appearing at 1570 cm^{-1} for Remazol red B, 1564 $cm^{-1}$for Golden yellow HER and 1565cm^{-1} for Amaranth. This is may further supported by the appearance of the band at 415-448 cm^{-1} due to metal- azo nitrogen stretching vibrations in the complexes[1]. The blue –shift of the γ (C-O) stretching band to the extent of (1155-1222 cm-1) in the complexes, confirms the involvement of the deprotonated OH group in chelating. This is further supported by the appearance of the band at 528-591 cm^{-1} due to metal- oxygen stretching vibrations in the complexes [2-6].

Ultraviolet-visible spectra.

The electronic spectra for dyes and its complexes recorded in EtOH are given in the Table 3.3.1-3.3.4. The electronic spectral date shows three bands in the region 218-258 nm (Fig.3.5-3.8.). When compared with the pure ligand spectrum, a shift in the bands is noticed, due to the formation of the complexes. A peak or shoulder in the region 260-475 nm can be assigned to the nitrogen (imino) to lead, cobalt, nickel and copper transitions. The band at 288 nm corresponds to n-π* and the one at 217-224 nm to π-π* transitions. A broad band around 680 nm is assigned to a d-d transition in the metal complexes[7-12].

EPR spectra.

The EPR spectra of copper complexes of dyes sample were recorded at 290 K using the original single TE102 (ER 4102 ST) rectangular cavity. The EPR spectra of copper complexes revealed presence of EPR signals, characterized by effective g-value of 2.0302, 2.0279, 2.0366 and 2.0419, Amaranth, Golden yellow HER, Methylene blue and Remazol red B respectively[13, 14] as is shown in Fig. 3.9.

Structure of the complexes

Since the structure of the metal complexes has been obtained, we characterized the complexes and determined its possible structure by elemental analysis, IR data, UV-vis and EPR measurements. The suggested structure of the complexes is shown in Fig.3.1.

Table .3.1.1

Analytical and physical data of metal complexes of Amaranth

Compound	Colour	Contents found(calculated) %					
		C	H	N	S	O	Metal
Lead complex of Amaranth	Dark green	33.97 (33.71)	1.43 (1.95)	3.96 (4.75)	13.60 (15.07)	22.63 (22.36)	14.65 (14.31)
Cobalt complex of Amaranth	Dark green	37.95 (35.49)	1.59 (2.20)	4.43 (3.44)	15.20 (15.02)	25.28 (26.01)	4.66 (4.60)
Nickel complex of Amaranth	Light green	37.96 (39.73)	1.59 (1.34)	4.43 (4.47)	15.20 (16.07)	25.28 (25.36)	4.64 (5.20)
Copper complex of Amaranth	Light green	37.81 (39.03)	1.59 (1.73)	4.41 (4.57)	15.14 (15.09)	25.19 (25.12)	5.00 (6.71)

Table .3.1.2

Analytical and physical data of metal complexes of Methylene blue

Compound	Colour	Contents found(calculated) %					
		C	H	N	S	O	Metal
Lead complex of Methylene blue	Red	49.53 (49.71)	4.08 (4.97)	10.83 (11.41)	8.26 (8.67)	-	26.76 (26.71)
Cobalt complex of Methylene blue	Brown red	61.23 (61.17)	5.78 (5.41)	13.39 (15.01)	10.22 (10.78)	-	9.39 (9.47)
Nickel complex of Methylene blue	yellow	61.25 (61.73)	5.78 (5.91)	13.39 (14.75)	10.22 (10.09)	-	9.35 (8.79)
Copper complex Methylene blue	Brown	60.78 (62.31)	5.74 (5.81)	13.29 (13.41)	10.14 (11.00)	-	10.03 (11.20)

Table .3.1.3

Analytical and physical data of metal complexes of Remazol red B

Compound	Colour	Contents found(calculated) %					
		C	H	N	S	O	Metal
Lead complex of Remazol red B	Rosy red	49.22 (49.15)	4.13 (1.37)	5.74 (5.95)	6.57 (6.75)	13.11 (13.25)	21.23 (25.41)
Cobalt complex of Remazol red B	Light red	58.03 (51.49)	4.87 (4.51)	6.77 (6.91)	7.75 (7.21)	15.46 (15.25)	7.12 (7.14)
Nickel complex of Remazol red B	Yellow orange	58.05 (59.11)	4.87 (4.91)	6.77 (6.91)	7.75 (7.91)	15.47 (16.01)	7.01 (7.73)
Copper complex Remazol red B	Orange	57.71 (59.17)	4.84 (4.95)	6.73 (6.10)	7.70 (7.21)	15.38 (15.36)	7.63 (6.95)

Table .3.1.4

Analytical and physical data of metal complexes of Golden yellow HER

Compound	Colour	Contents found(calculated) %					
		C	H	N	S	O	Metal
Lead complex of Golden yellow HER	Red brown	56.12 (56.07)	6.12 (5.98)	9.92 (9.36)	-	3.74 (3.52)	24.15 (24.23)
Cobalt complex of Golden yellow HER	Orange brown	67.87 (65.98)	7.40 (7.25)	11.87 (11.36)	-	4.52 (4.69)	8.33 (8.12)
Nickel complex of Golden yellow HER	Yellow red	67.90 (67.48)	7.41 (7.15)	11.88 (11.36)	-	4.52 (4.56)	8.30 (8.12)
Copper complex of Golden yellow HER	Pale red	67.44 (67.11)	7.36 (7.23)	11.80 (11.23)	-	4.49 (4.36)	8.92 (8.59)

Table .3.2.1

Selected IR data (4000-400 cm^{-1}) of Amaranth and its metal complexes

Compound	γ(C=N)	γ (N=N)	γ (C=O)	γ (M-O)	γ (M-N)	γ (M-N)$_{Azo}$
Amaranth	-	1565	1171	-	-	-
Lead complex of Amaranth	-	1564	1209	577	-	421
Cobalt complex of Amaranth	-	1570	1222	528	-	434
Nickel complex of Amaranth	-	1557	1201	561	-	435
Copper complex of Amaranth	-	1563	1159	570	-	440

Table .3.2.2

Selected IR data (4000-400 cm^{-1}) of Methylene blue and its metal complexes

Compound	γ(C=N)	γ (N=N)	γ (C=O)	γ (M-O)	γ (M-N)	γ (M-N)$_{Azo}$
Methylene blue	1576	-	-	-	-	-
Lead complex of Methylene blue	1617	-	-	-	445	-
Cobalt complex of Methylene blue	1627	-	-	-	449	-
Nickel complex of Methylene blue	1632	-	-	-	510	-
Copper complex Methylene blue	1636	-	-	-	519	-

Table .3.2.3

Selected IR data (4000-400 cm^{-1}) of Remazol red B and its metal complexes

Compound	γ(C=N)	γ (N=N)	γ (C=O)	γ (M-O)	γ (M-N)	γ $(M-N)_{Azo}$
Remazol red B	-	1570	1203	-	-	-
Lead complex of Remazol red B	-	1629	1188	580	-	420
Cobalt complex of Remazol red B	-	1631	1171	582	-	432
Nickel complex of Remazol red B	-	1637	1155	578	-	415
Copper complex Remazol red B	-	1563	1205	591	-	448

Table .3.2.4

Selected IR data (4000-400 cm^{-1}) of Golden yellow HER and its metal complexes

Compound	γ(C=N)	γ (N=N)	γ (C=O)	γ (M-O)	γ (M-N)	γ $(M-N)_{Azo}$
Golden yellow HER	-	1564	1198	-	-	-
Lead complex of Golden yellow HER	-	1562	1207	580	-	435
Cobalt complex of Golden yellow HER	-	1587	1208	545	-	440
Nickel complex of Golden yellow HER	-	1560	1198	560	-	436
Copper complex of Golden yellow HER	-	1564	1206	572	-	421

Table.3.3.1

Electronic bands of Amaranth and its metal complexes.

Compound	Maximum wavelength (nm)
Amaranth	238,243,325
Lead complex of Amaranth	265,294,475
Cobalt complex of Amaranth	265,294,475
Nickel complex of Amaranth	239,260,475
Copper complex of Amaranth	254,325,594

Table.3.3.2

Electronic bands of Methylene blue and its metal complexes.

Compound	Maximum wavelength (nm)
Methylene blue	268,282,513
Lead complex of Methylene blue	248,308,479
Cobalt complex of Methylene blue	235,395,439
Nickel complex of Methylene blue	246,331,667
Copper complex Methylene blue	242,331,614

Table.3.3.3

Electronic of Remazol red B and its metal complexes.

Compound	Maximum wavelength (nm)
Remazol red B	217,311,613
Lead complex of Remazol red B	238,329,477
Cobalt complex of Remazol red B	239,310,483
Nickel complex of Remazol red B	212,331,620
Copper complex Remazol red B	224,350,

Table.3.3.4

Electronic bands of Golden yellow HER and its metal complexes.

Compound	Maximum wavelength (nm)
Golden yellow HER	247,321,471
Lead complex of Golden yellow HER	224,350,412
Cobalt complex of Golden yellow HER	218,308,620
Nickel complex of Golden yellow HER	247,332,613
Copper complex of Golden yellow HER	228,337,605

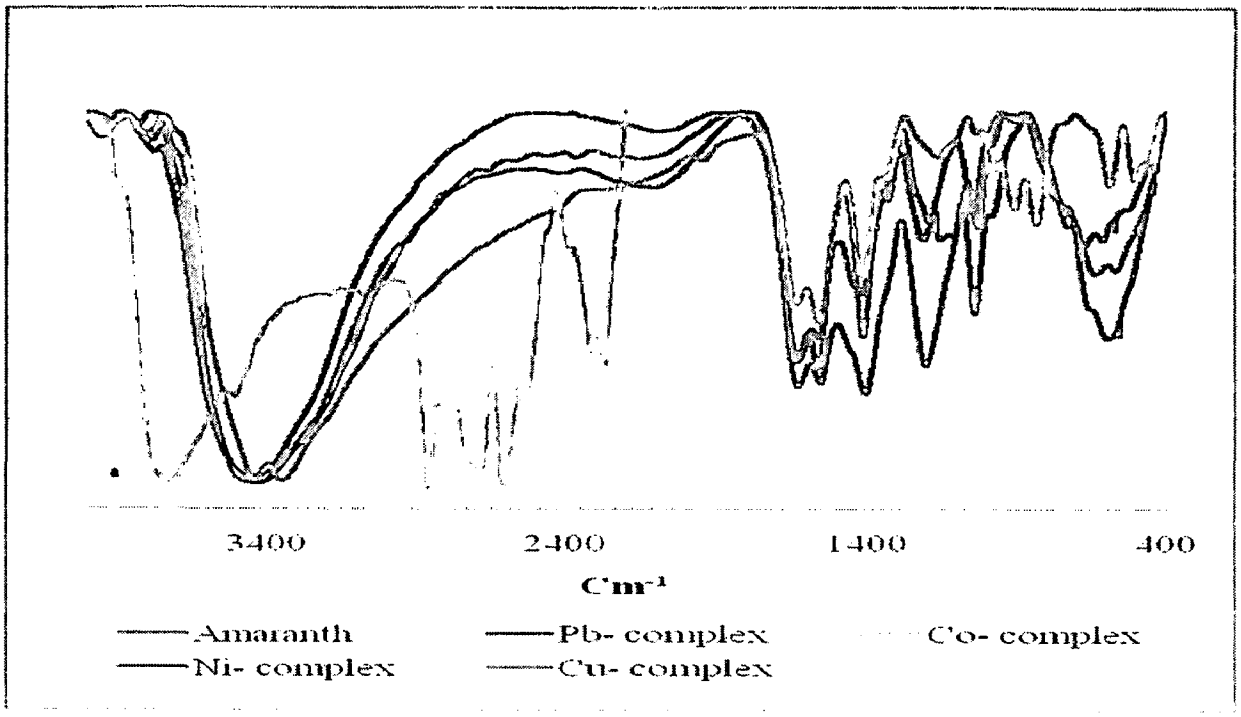


Fig3.1 . IR spectral data of Amaranth and its complexes.

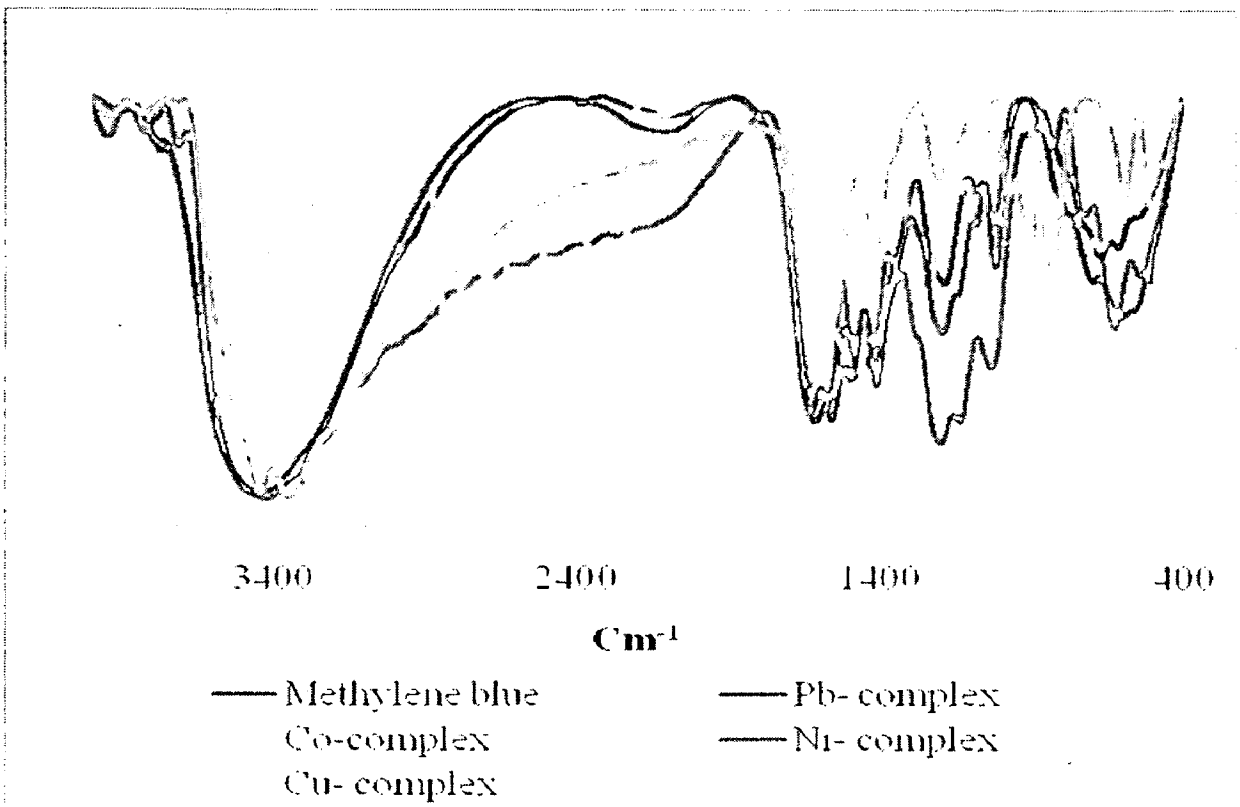


Fig.3.2. IR spectra of Methylene blue and its complexes.

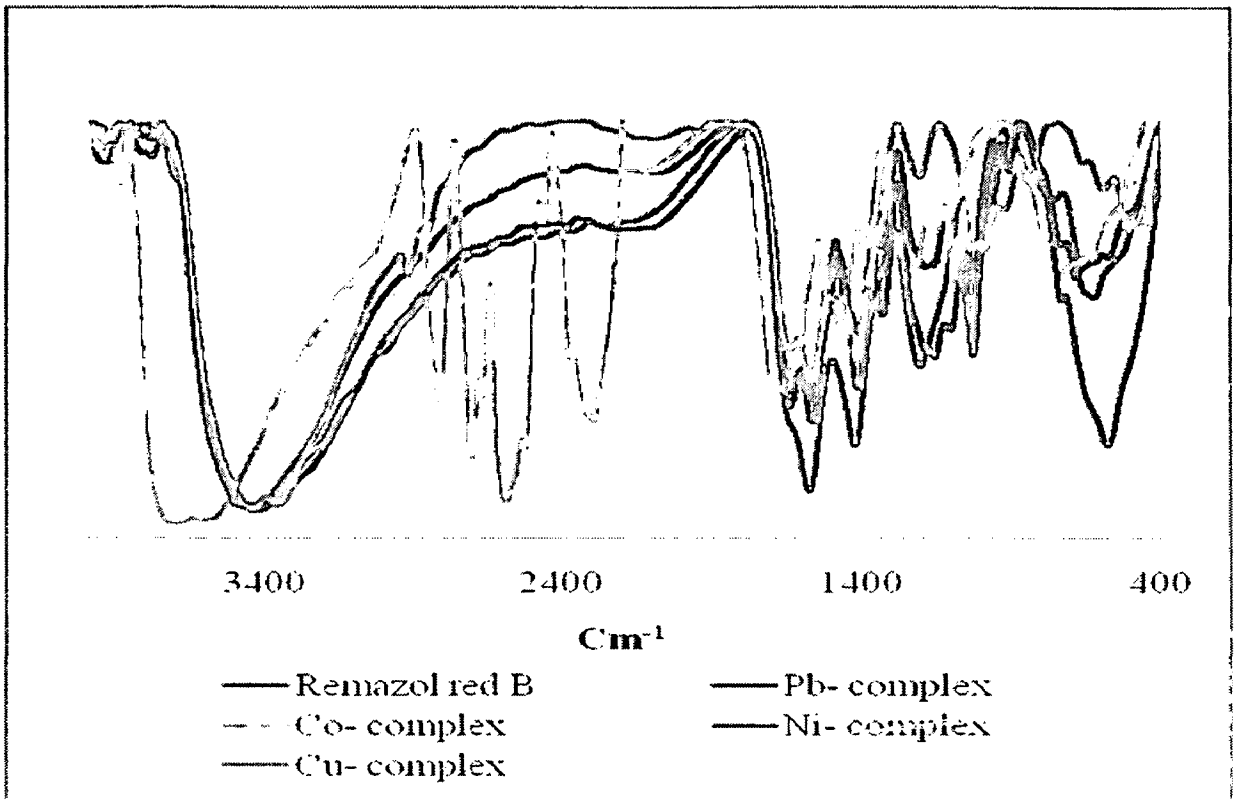


Fig.3.3. IR spctra of Remazol red B and its complexes.

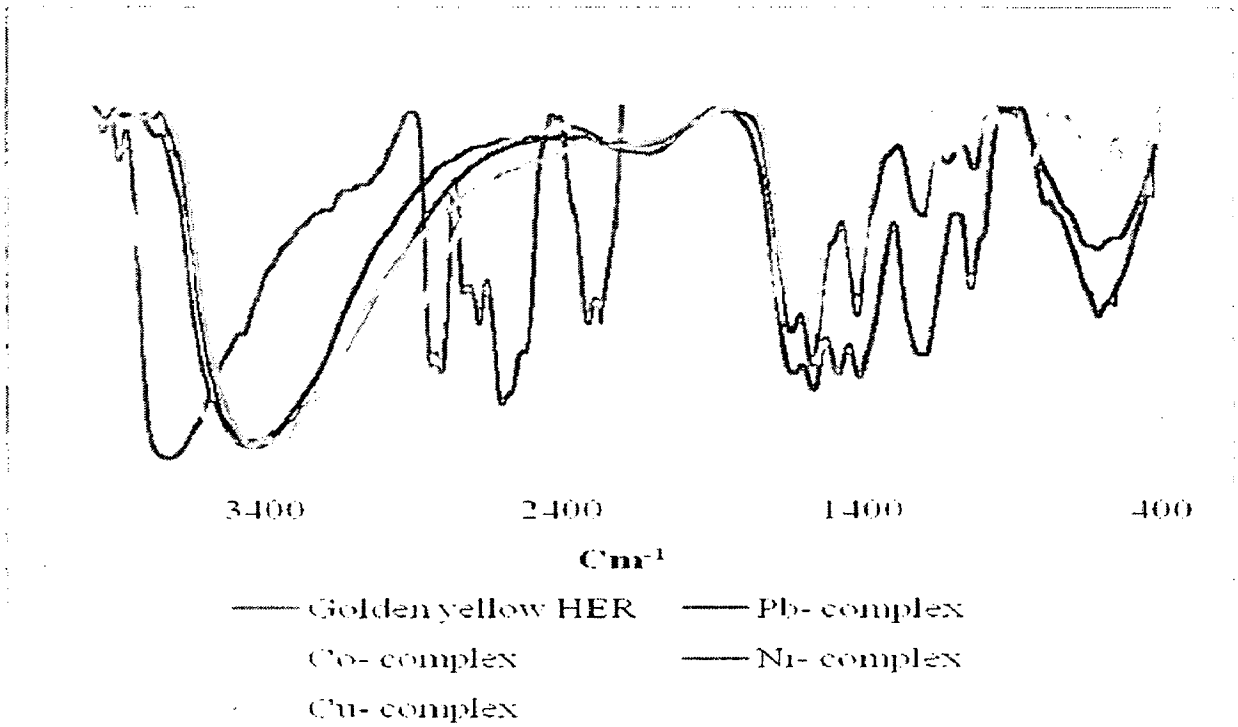


Fig.3.4. IR spectra of Golden yellow HER and its complexes.

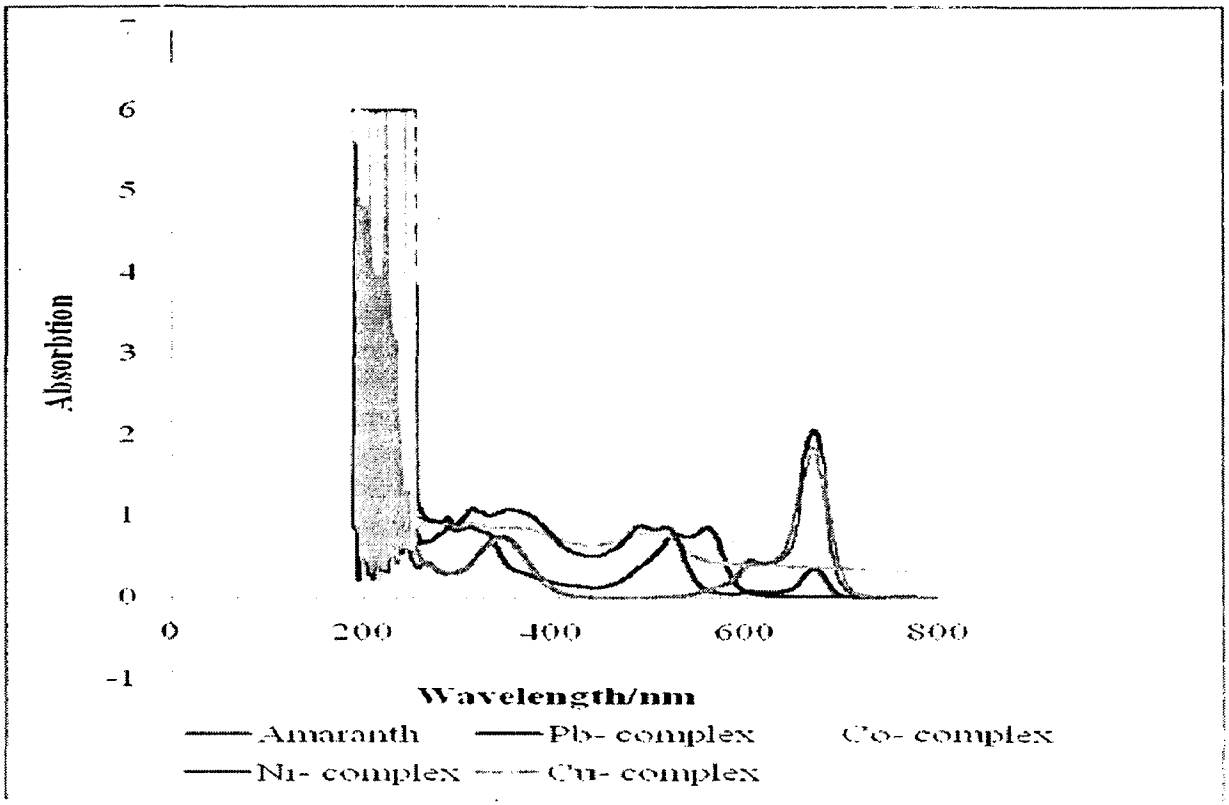


Fig3.5. UV spectral data of Amaranth and its complexes.

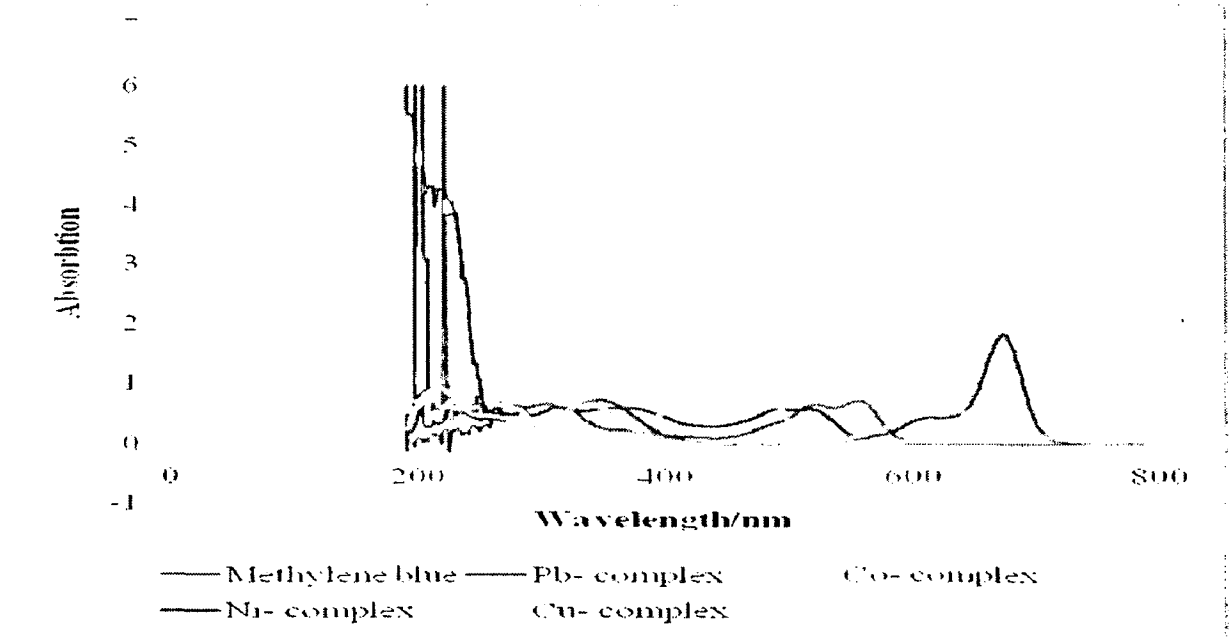


Fig3.6. UV spectral data of Methylene blue and its complexes.

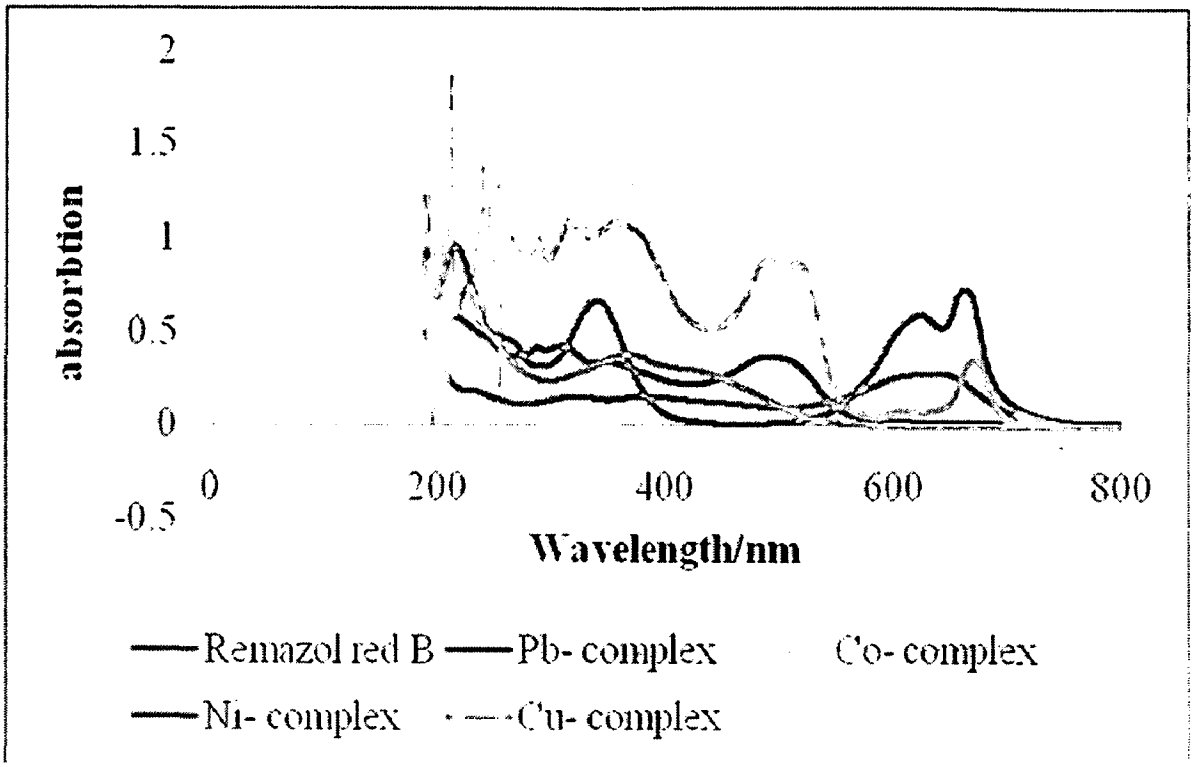


Fig3.7. UV spectral data of Remazol red B and its complexes.

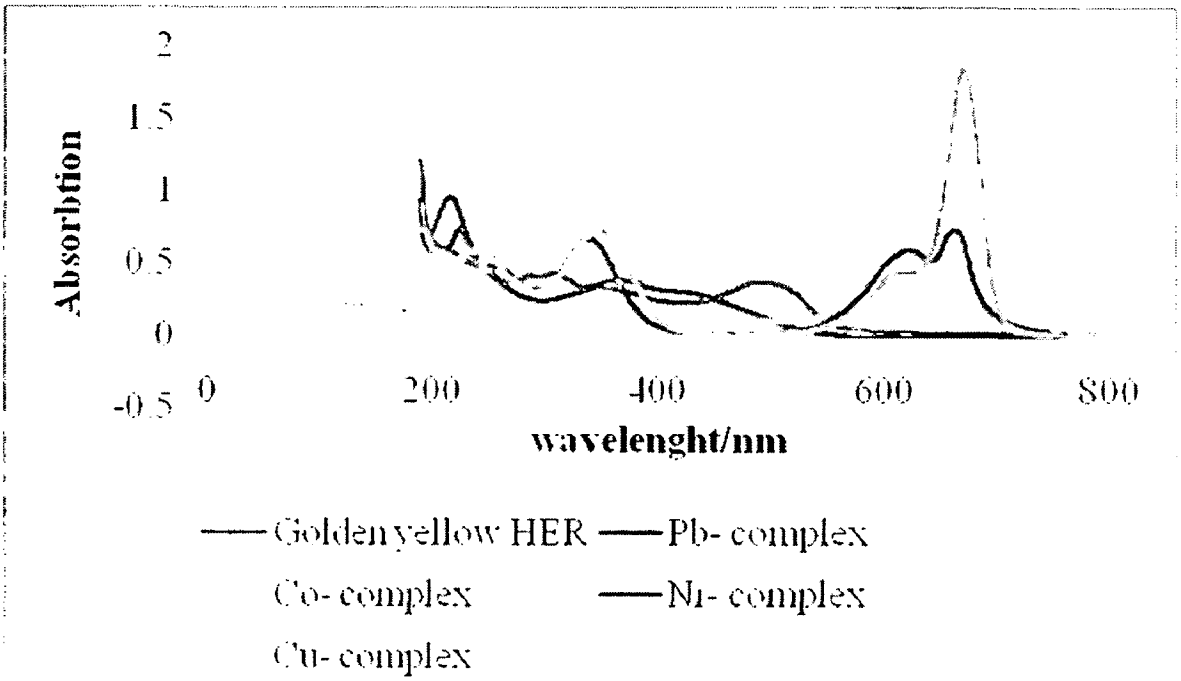


Fig3.8. UV spectral data of Golden yellow HER and its complexes.

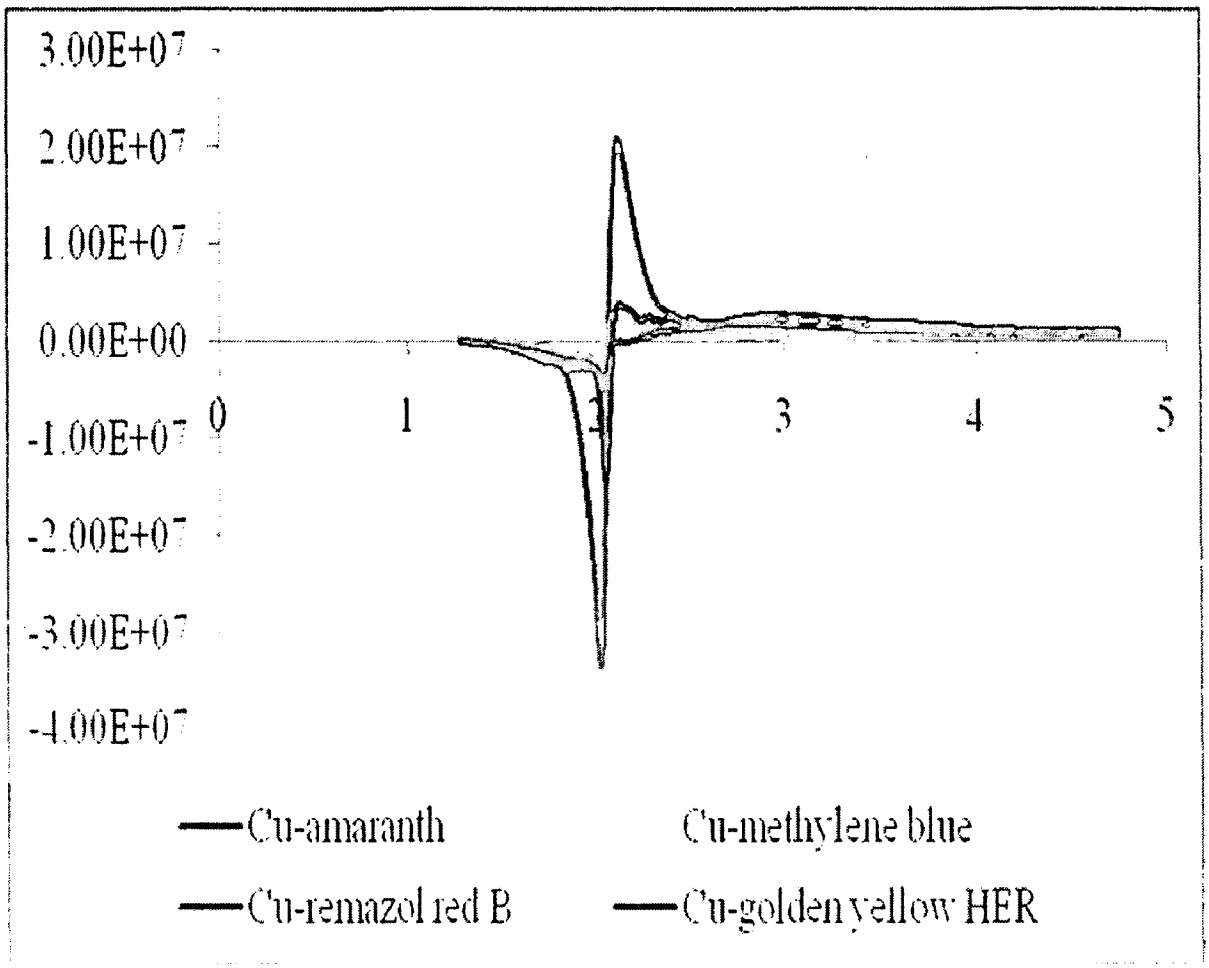
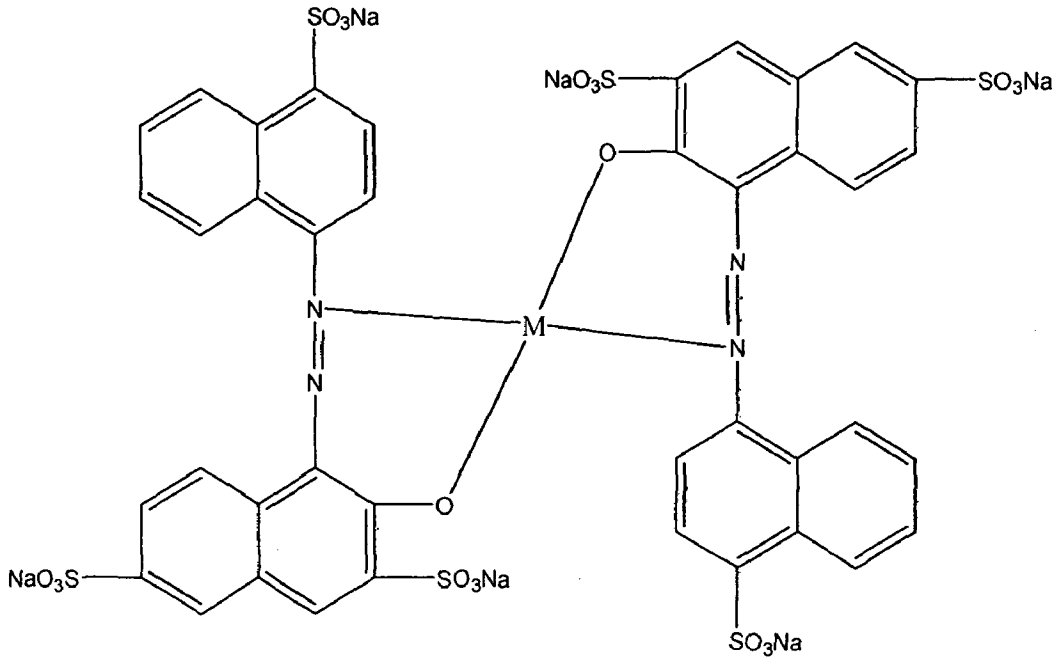
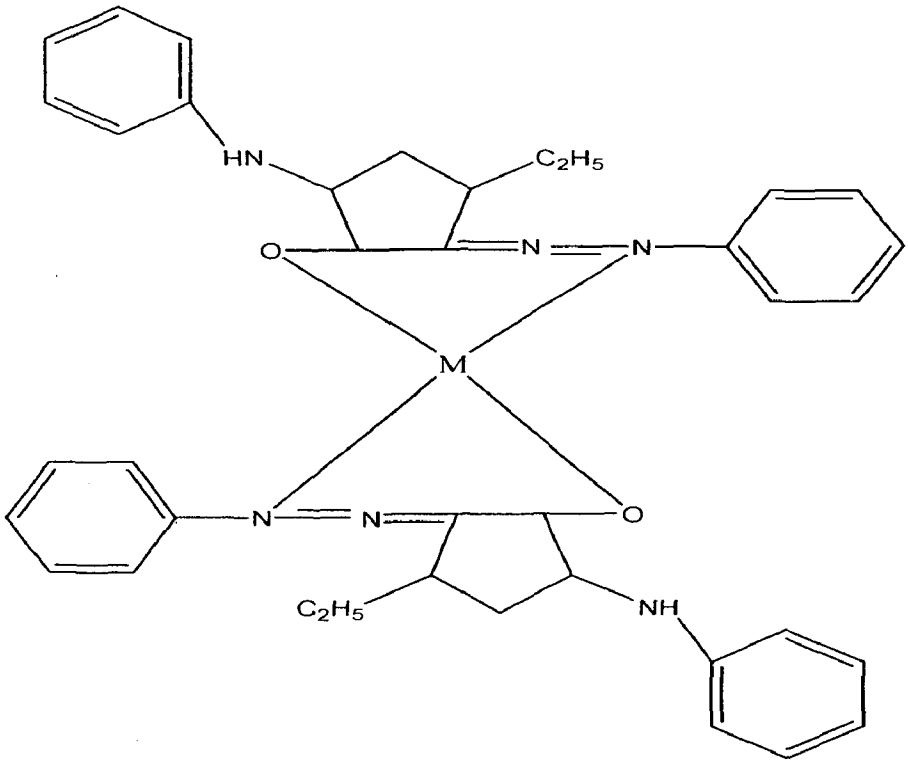


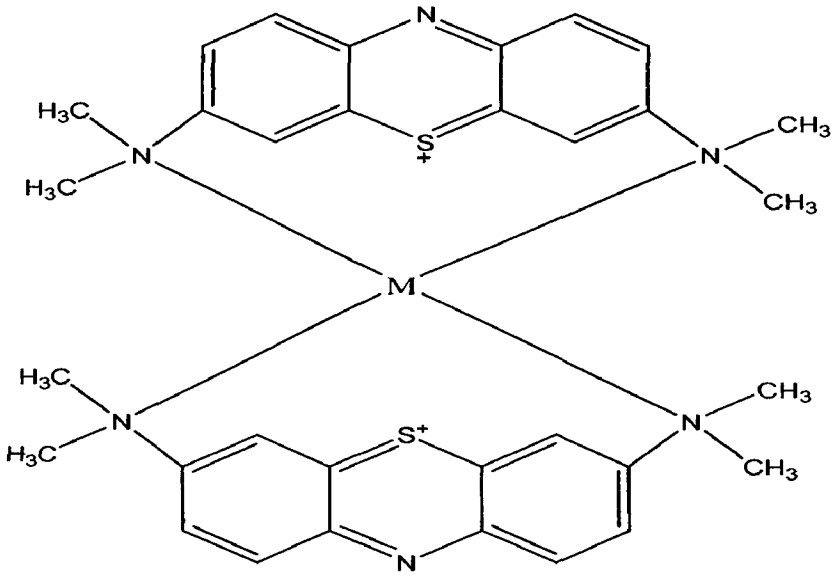
Fig3.9. EPR spectral data of copper complexes.



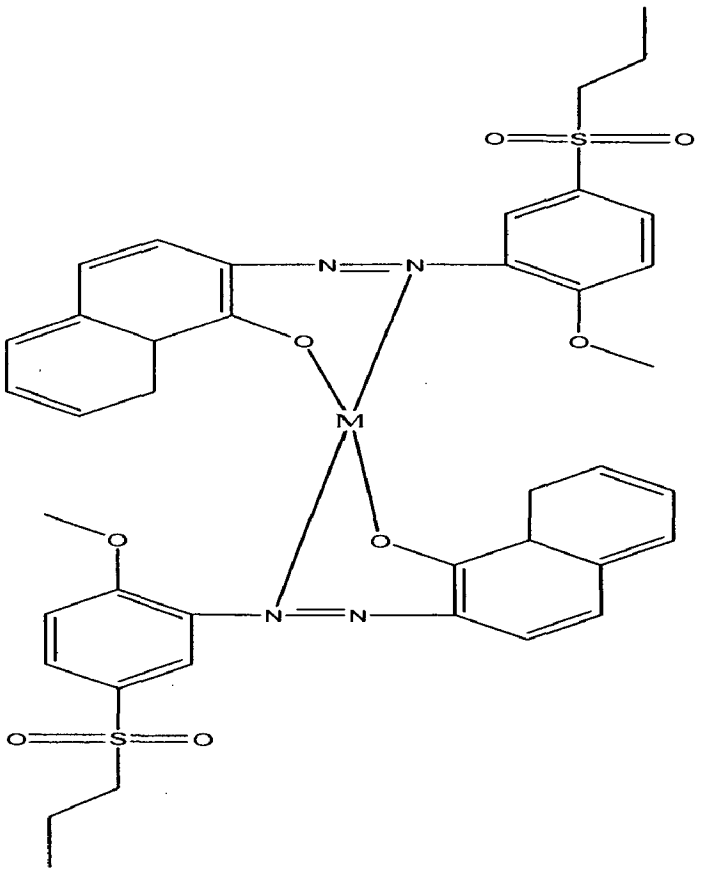
M=Pb,Co,Ni and Cu



M=Pb.Co,Ni and Cu



M=Pb,Co,Ni and Cu



M= Pb,Co,Ni and Cu

Fig.3.1 The suggested structure of the complexes.

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