

## Spectral studies of Organic Marine dye with Cu(II), Ni(II), Zn(II) and Pb(II) metal complexes

Jayandran M <sup>a, \* 1</sup>, Balasubramanian V <sup>b, 2</sup>

<sup>a</sup> Department of Chemistry, Mahendra Engineering College, Namakkal, India

<sup>b</sup> Department of Chemistry, AMET University, Chennai, India

[jayandranchem@gmail.com](mailto:jayandranchem@gmail.com)

### Abstract

The organic dye compound like 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium dye compound was synthesized by taking 4-amino-3, 6-bis((4-((4-chloro-6-((3-sulfophenyl)amino)-1, 3, 5-triazin-2-yl)amino)-2-sulfophenyl)azo)-5-hydroxy group, and hexasodium salt reacted with -2, 7-Naphthalenedisulfonic acid, are used to synthesized dye like hexasodium salt reactive green-19 Dyes ( $C_{40}H_{23}C_{12}N_{15}O_{19}S_6.6Na$ ). It is soluble in water. The crystals of 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2,7-naphthalene disulfonic acid hexasodium dye compound have been grown by diluting the substances with slow evaporation technique. The grown crystals were characterized by powder crystal X-ray diffraction (XRD) analysis, FTIR studies, UV-visible transmittance studies and The Carbon, hydrogen, nitrogen and sulphur (CHNS) analyses the metal complexes of dye with  $M^{2+}$  were performed using CHN analyzer. The EPR for special studies due to Cu (II) metal. The morphology analysis of the metal complexes of dye with  $M^{2+}$  is carried out through Scanning Electron Microscopy with Energy Dispersive Spectrometer (SEM with EDS), its magnification was 5 X 3, 00, 000 times with a resolution of 3 nm. All these analysis are successfully reported as the dye with strong metal coordination complex formation.

**Keywords:** crystal growth; FTIR; UV; Powder XRD; SEM with EDS and dyes with Metal-Coordination complexes.

## 1. Introduction

Colours have played an important role in the life of human beings. Dyes and pigments are very important articles in commerce since time immemorial. Dye substances are used for the purpose of coating various metals used in textile and dyeing fields. Dyes must have a suitable colouring agent for the coating purpose of metal surface and it must be capable of attaching with the suitable materials. Previously dyes originated from animal and vegetable sources, but nowadays most of the available dyes are synthetic dyes which are prepared from various organic compounds [1]. The dye compound like 4-amino-3, 6-bis [[4-[[4-chloro-6-[(3-sulfophenyl) amino]-1, 3, 5-triazin-2-yl] amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium compound was reported the details of crystal structure and its coordinate structure with metal complexes. Hence the plan of this present paper is to be report the crystal growth, metal complexes and spectroscopic studies like powder crystal X-ray diffraction (XRD) analysis, FTIR studies, UV-visible transmittance studies and The Carbon, hydrogen, nitrogen and sulphur (CHNS) analyses the metal complexes of dye with  $M^{2+}$  were performed using CHN analyzer. The EPR for special studies due to Cu (II) metal. The morphology analysis of the metal complexes of dye with  $M^{2+}$  is carried out through Scanning Electron Microscopy –Energy (SEM with EDS) of 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl] azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium compound for the first time. Recently the present electrochemical studies of this complexes work have never been reported else were.

## 2. Materials and Methods

### 2.1 Spectral Analysis of Crystallized Dye

The Fourier Transform Infrared (FTIR) spectrum of 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2,7-naphthalene disulfonic acid hexasodium dye crystal was recorded in the region 400 - 4000  $cm^{-1}$  using FTIR

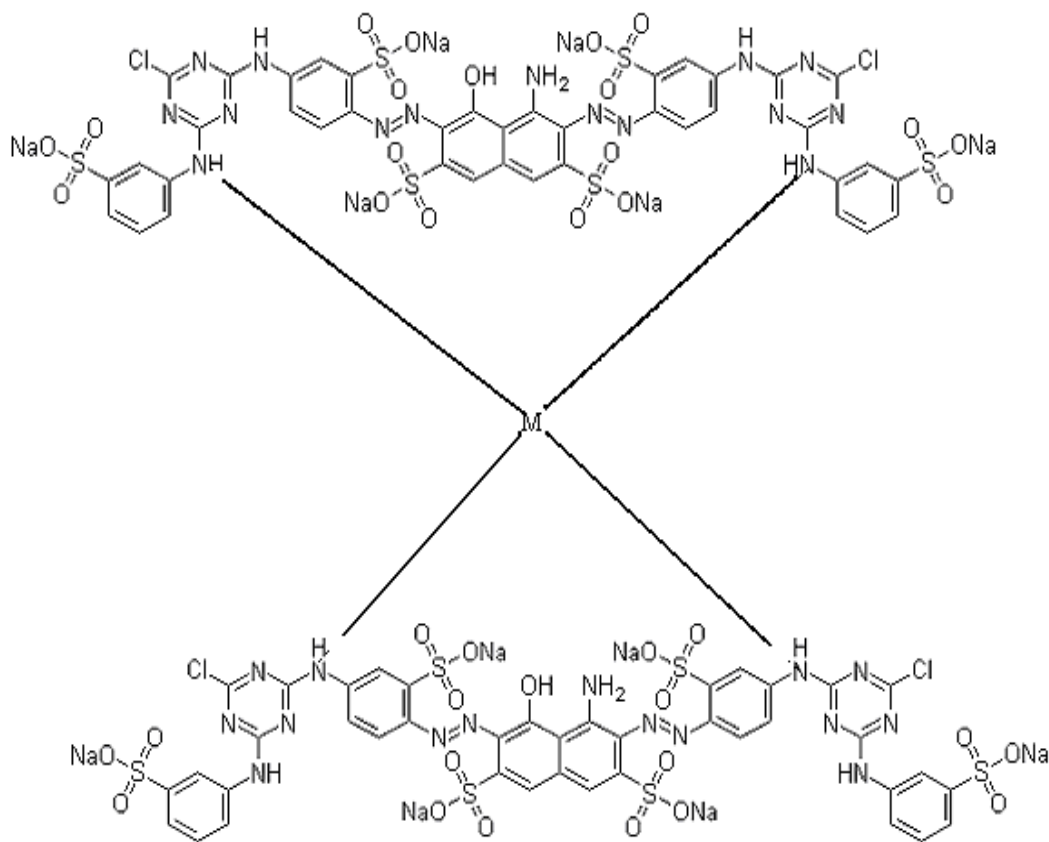
SHIMADZU 8400S and the UV-Visible transmittance spectrum was recorded in the wavelength range 200-1200 nm, using Lambda 35 spectrometer. The grown crystals were subjected to crystal XRD to confirm the crystallinity and also to estimate the lattice parameters by employing Bruker-Nonious MACH3/CAD4 Powder X-ray diffractometer and the Surface analysis was carried out through Scanning Electron Microscopy in the high magnification of 500 times has been studied for this crystal by the equipment JEOL Model JSM - 6390LV maximum magnification studied in the Magnification is 5 X 3, 00, 000 times with a resolution of 3 nm are recorded.

## 2.2 Preparation of the Dyes with Metal Complexes

4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfo phenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium dyes with  $M^{2+}$  ( $Cu(OAc)_2$ ,  $NiNO_3$ ,  $PbNO_3$  and  $ZnSO_4$ ). The metal complexes of 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2,7-naphthalene disulfonic acid hexasodium dye with  $M^{2+}$  (Figure-1) were prepared by the following general procedure, a hot methanolic solution (100 ml) of the ligand, a methanolic solution of metal (II) salt like  $Cu(OAc)_2$  was added in 1:1 molar ratio. The pH of the solution was adjusted to 6.5–7.0 and refluxed on a water-bath for 4 hrs. Then the reaction mixture was concentrated to half its initial volume by evaporation. On cooling the solution, the complex separated out was filtered, washed successively with methanol and ether and finally dried in vacuum over  $P_4O_{10}$ .

All the chemicals were used of Analytical grade. For physico-chemical measurements, the solvents were purified by standard methods. X-ray diffraction experiments were carried out on a Anton Paar, TTK 450 Temperature Range :- 170 °C to +450 °C The D8 Advance X-ray Diffractometer can be used for all X-ray powder diffraction applications such as structural analysis of the metal complexes of 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfo phenyl]

azo]-5-hydroxy-2,7-naphthalenedisulfonic acid hexasodium dye with  $M^{2+}$  crystalline solids, determination of unit-cell parameters, determination of crystal morphology.



**Figure-1: 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2,7-naphthalenedisulfonic acid hexasodium dye compound with  $M^{2+}$**

The Carbon, hydrogen, nitrogen and sulphur (CHNS) analyses the metal complexes of 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2,7-naphthalenedisulfonic acid hexasodium dye with  $M^{2+}$  were performed using Elementar Systeme Vario EL III CHN analyzer. The electronic spectra of the metal complexes of 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-

2,7-naphthalenedisulfonic acid hexasodium dye with  $M^{2+}$  were recorded on a Hitachi 320 UV-vis spectrophotometer. Fourier Transform Infra Red Spectrometer (FTIR) spectral studies of the metal complexes of 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2,7-naphthalene disulfonic acid hexasodium dye with  $M^{2+}$  were carried out using KBr discs on a Thermo Nicolet, Avatar 370 Spectral range :4000-400  $cm^{-1}$  Resolution :4  $cm^{-1}$  KBr beam splitter DTGS Detector HATR Assembly for convenience of measurement spectrophotometer. The EPR spectrum of the copper (II) complex was recorded in the solid state and also in DMSO at liquid nitrogen temperature using a Varian E-112 EPR spectrometer employing DPPH as reference material. Surface analysis of the metal complexes of 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2,7-naphthalenedisulfonic acid hexasodium dye compound with  $M^{2+}$  is carried out through Scanning Electron Microscopy –Energy Dispersive Spectrometer(EXM-EDX), The magnification 500 times has been studied for this crystal by the equipment JEOL Model JSM - 6390LV maximum magnification studied in the Magnification is 5 X 3, 00, 000 times with a resolution of 3 nm [2,3].

### 3. RESULTS AND DISCUSSION

#### 3.1 CHNS ANALYSIS OF DYES WITH METAL COMPLEXES

The instrumental techniques and characterization of dyes (4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalene disulfonic Acid Hexasodium dye compound, and its complexes like  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  are described in this chapter. Elemental analysis of dyes and metal complexes are shown in (Table.1) all cases 1:2 (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 (Figure-2) are a bidentate ligand with nitrogen,

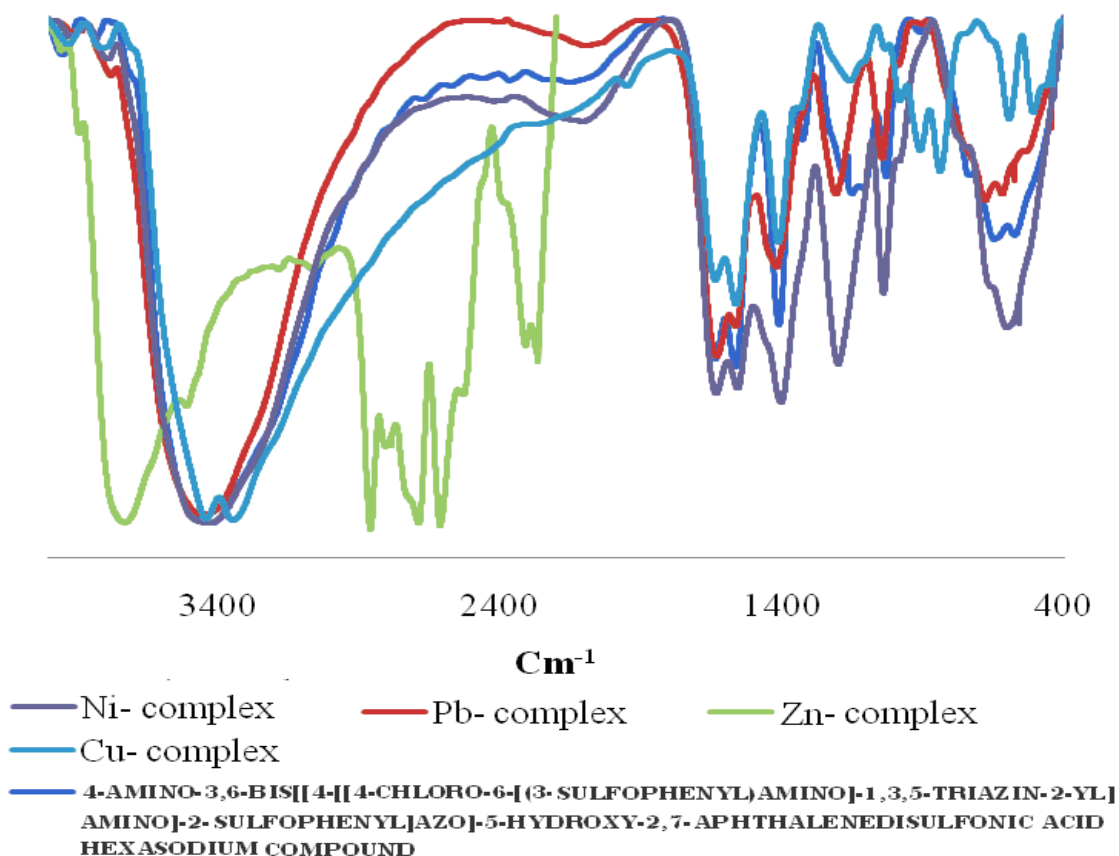
azo nitrogen and hydroxyl oxygen as the coordination site which usually forms 1:2 metal: ligand, chelates. All the complexes and the ligand are coloured, soluble in DMSO and DMF.

**Table 1: Analytical and physical data of metal complexes of 4-Amino-3,6-Bis[[4-[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalene disulfonic Acid Hexasodium Compound**

Compound	Colour	Contents found(calculated) %					
		C	H	N	S	O	Metal
Lead complex of 4-Amino-3,6-Bis[[4-[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound	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)
Zinc complex of 4-Amino-3,6-Bis[[4-[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound	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 4-Amino-3,6-Bis[[4-[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound	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 4-Amino-3,6-Bis[[4-[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound	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)

### 3.5 Fourier Transforms Infrared (FTIR) Spectroscopy

The FTIR spectra of the dyes and its complexes were recorded in the region of 400-4000 $\text{cm}^{-1}$  range and using KBR pellet (Table-2). FTIR spectra of the ligand show a broad at 3936  $\text{cm}^{-1}$  due to the OH groups (Figure-2). In the metal complexes, this broad band is still broad due to other groups. The stretching vibration of the phenothiazine  $\gamma$  (C=N) is observed in the form of an intense band at 1576  $\text{cm}^{-1}$  in the free ligand. The involvement of the deprotonated  $\gamma$  (C-N) disodium naphthanol (4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfo phenyl]Azo]-5-Hydroxy-2,7-Naphthalene disulfonic Acid Hexasodium dye compound.



**Figure-2 FTIR of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfo phenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium with metal complexes.**

The spectra region at  $1650\text{ cm}^{-1}$  is complicated because of the stretching modes of  $\text{C}=\text{C}$  and  $\text{N}=\text{N}$ - which are superimposed in the same region. However, the band appearing at  $1565\text{ cm}^{-1}$  for 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium compound. This is may further supported by the appearance of the band at  $415\text{-}448\text{ cm}^{-1}$  due to metal-azo nitrogen stretching vibrations in the complexes. The blue shift of the  $\gamma$  (C-O) stretching band to the extent of ( $1155\text{-}1222\text{ cm}^{-1}$ ) in the complexes, confirms the involvement of the deprotonated OH group in chelating. This is further supported by the appearance of the band at  $528\text{-}591\text{ cm}^{-1}$  due to metal-oxygen stretching vibrations in the complexes [4-6].

**Table-2: Selected FTIR data ( $4000\text{-}400\text{ cm}^{-1}$ ) of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalene disulfonic Acid Hexasodium Compound and its metal complexes**

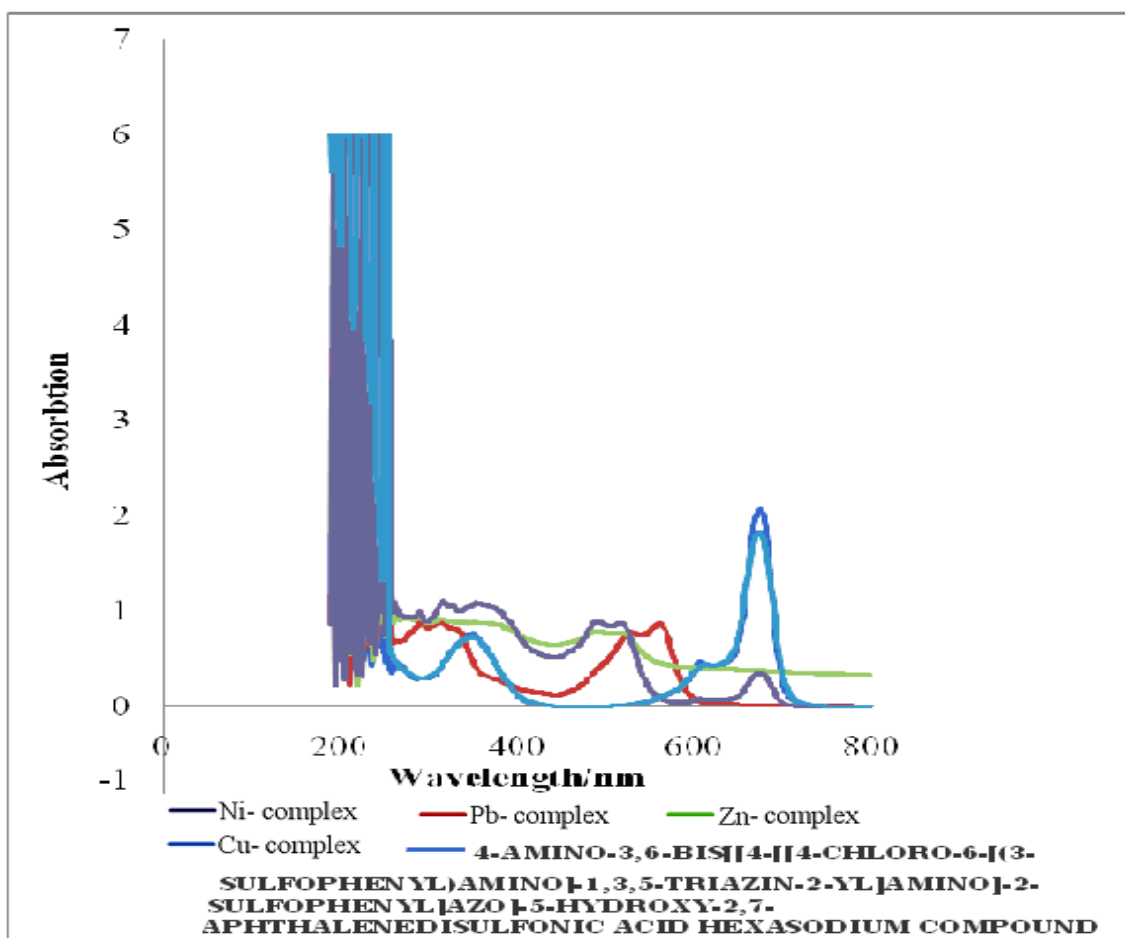
Compound	$\gamma(\text{C}=\text{N})$	$\gamma(\text{N}=\text{N})$	$\gamma(\text{C}=\text{O})$	$\gamma(\text{M}-\text{O})$	$\gamma(\text{M}-\text{N})$	$\gamma(\text{M}-\text{N})_{\text{Azo}}$
4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium	-	1565	1171	-	-	-
Lead complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium	-	1564	1209	577	-	421
Zinc complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium	-	1570	1222	528	-	434
Nickel complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-	-	1557	1201	561	-	435



Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium						
Copper complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium	-	1563	1159	570	-	440

### 3.6 Ultraviolet-Visible Spectra

The electronic spectral data shows three bands in the region 218-258 nm (Figure-3). When compared with the pure ligand spectrum, a shift in the bands is noticed, due to the formation of the dyes complexes are shown in Table-3. A peak or shoulder in the region 260-475 nm can be assigned to the nitrogen (imino) to lead, Zinc, nickel and copper transitions. The band at 288 nm corresponds to  $n-\pi^*$  and the one at 217-224 nm to  $\pi-\pi^*$  transitions. A broad band around 680 nm is assigned to a d-d transition in the metal complexes [7-9].



**Figure 3: UV spectral data of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-triazin-2-yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound and its metal complexes**

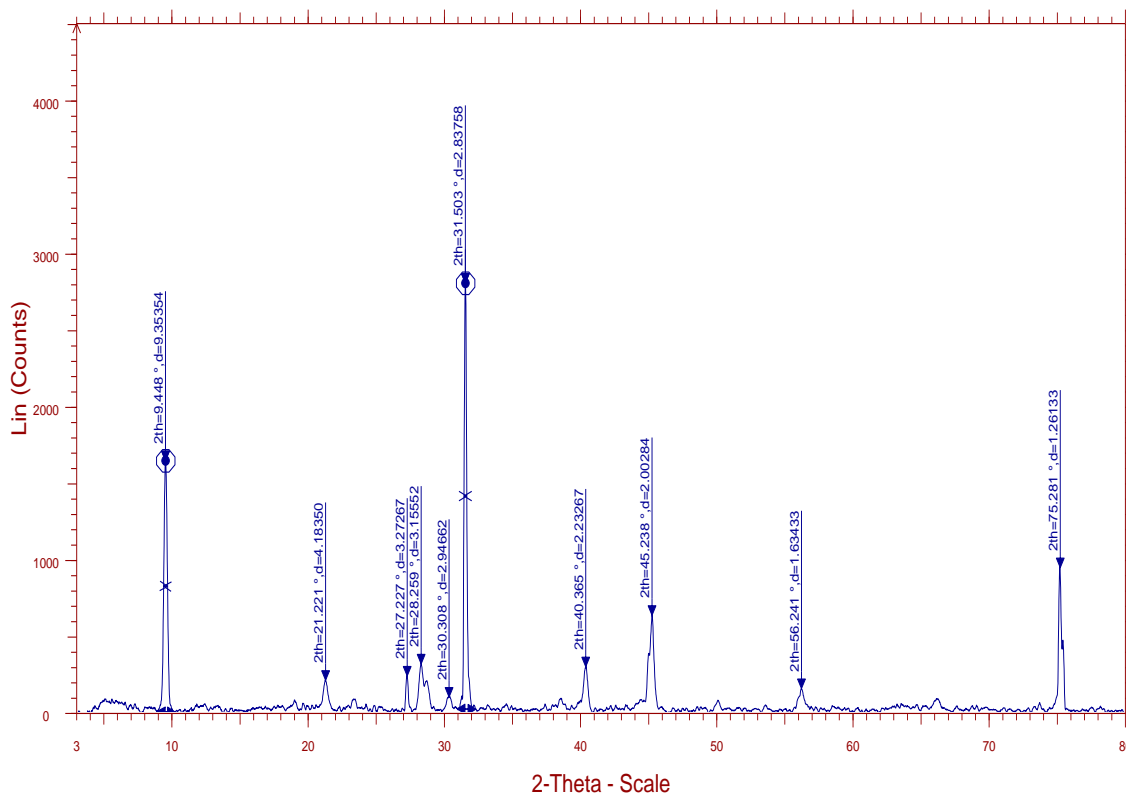
**Table-3: Electronic bands of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfo phenyl) Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalene disulfonic Acid Hexasodium Compound and its metal complexes.**

Compound	Maximum wavelength (nm)
4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound	238,243,325
Lead complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound	265,294,475
Zinc complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound	265,294,475
Nickel complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound	239,260,475
Copper complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound	254,325,594

### 3.7 XRD Analysis Dyes with Ni Complex

4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Salt (Reactive Green-19) Crystal With Ni Complex. The XRD pattern obtained for the complex formed with 4-amino-3,6-

bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2,7-naphthalene disulfonic acid dye with Ni is shown in Figure-4.

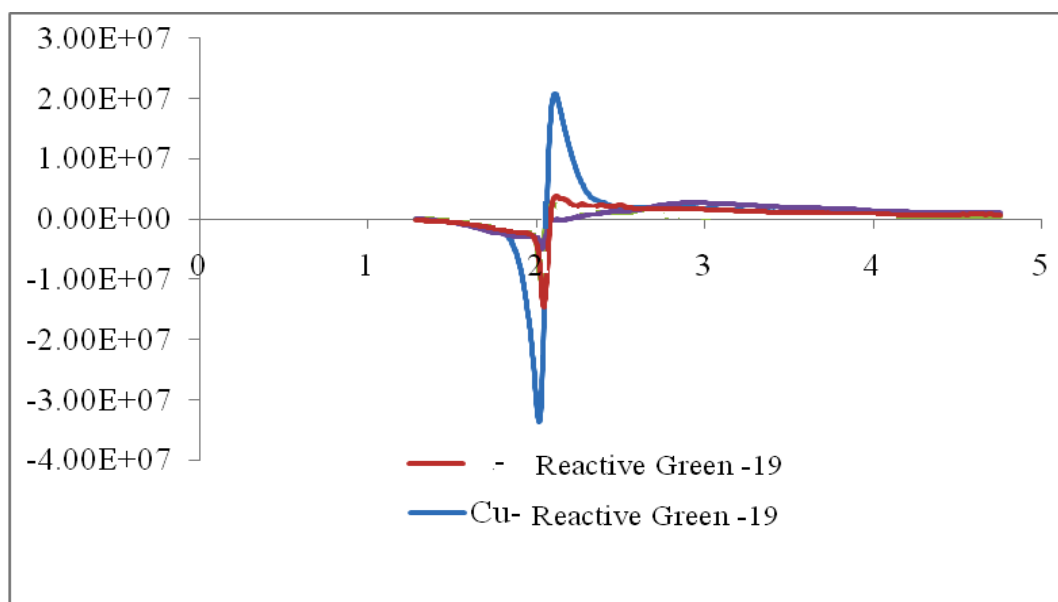


**Figure-4: XRD patterns recorded from 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2,7-naphthalene disulfonic acid hexasodium crystal with Ni Complex**

The pattern reveals the successful formation of the above said complex, which is evident from the characteristic peaks. The obtained pattern was also matched with standard diffraction pattern, which shows an excellent agreement with the standard data. The peak height is an indicative of the amount of crystallinity and it is evident from the figure that the sample possesses excellent crystallinity. Moreover the peak width observation indicates that the size of the particles could be around the micrometer range owing to the narrow sized peaks.

### 3.8 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[10,11]. The EPR spectra of copper complexes revealed presence of EPR signals, characterized by effective g-value (2.0302) of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl] Azo]-5-Hydroxy-2,7-NaphthalenedisulfonicAcid Hexasodium compound shown in Figure-5.



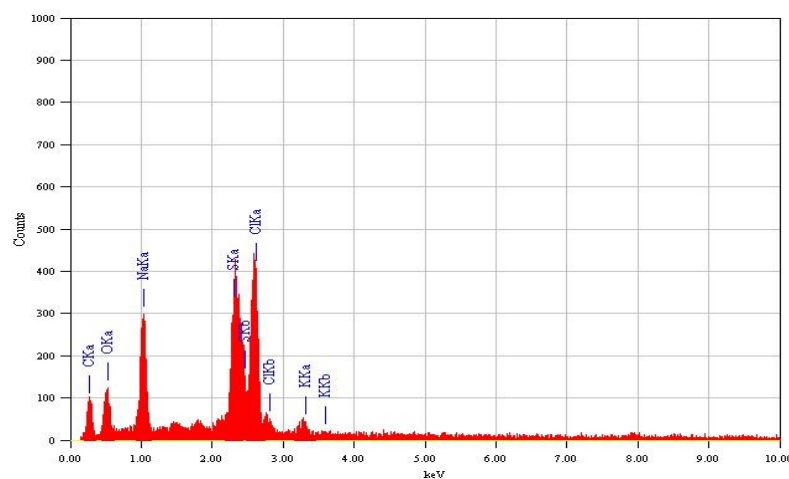
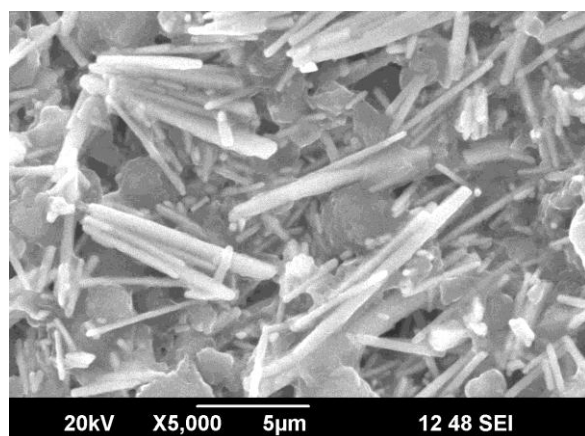
**Figure-5: EPR spectral data of 4-Amino-3, 6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]- 1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalene disulfonicAcid Hexasodium dye with copper complexes**

### 3.9 SCANNING ELECTRON MICROSCOPE with ENERGY DISPERSIVE X-RAY

#### SPECTROMETER (SEM with EDS)

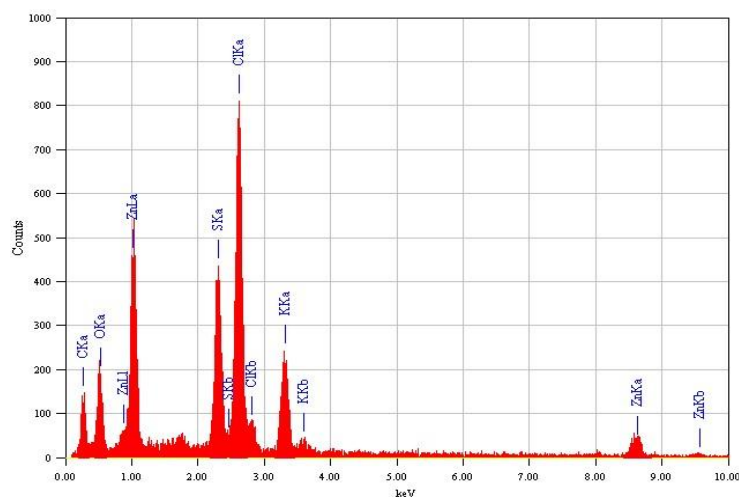
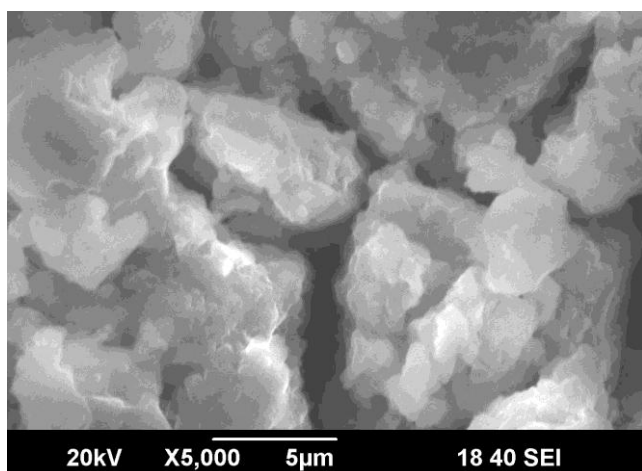
SEM studies reveal the change in the morphology of particles and homogeneity of the product. Even if there is a clear difference in the crystallization state of the metallo dyes sample like 4-Amino-

3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium of lead, Zinc, nickel and copper complexes and the corresponding EDAX are also given. As an illustration of many of these SEM images obtained with magnification of x 5000 a big size elliptic particle [12-16]. Semi quantitative estimation of major and minor elements present in the samples has been done under SEM, along with EDAX Shown Figure-6-9. The energy value of each peak may be matched with X-ray emission wavelength for non-diffractive analysis and the elements present in metallo dyes (except Lead and Zinc complexes due to their low percentage).



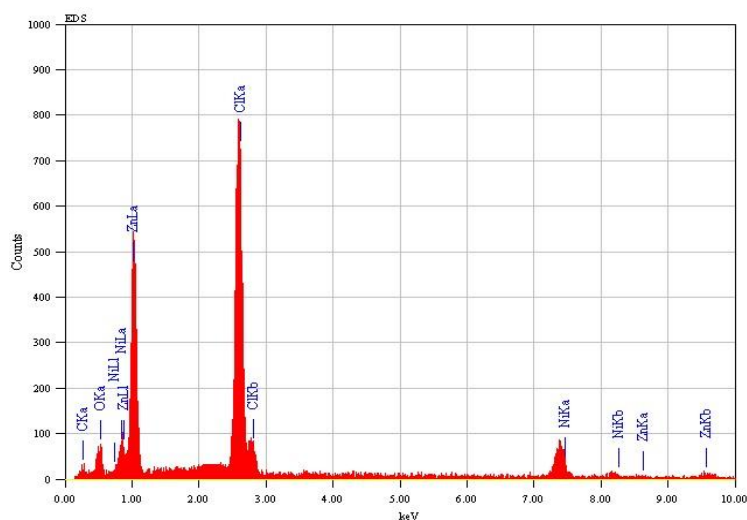
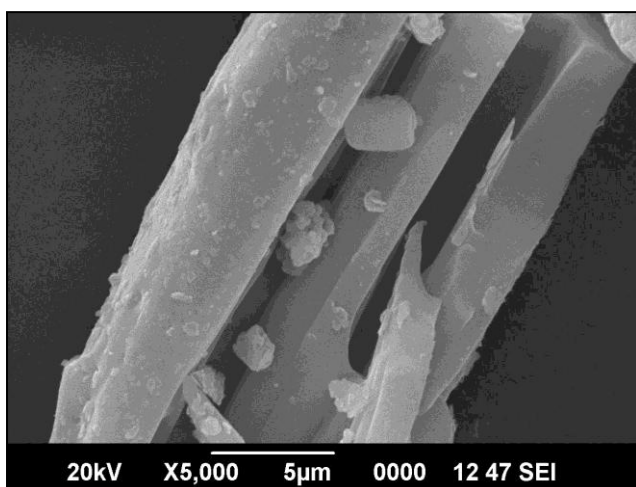
(a)

**Figure-6: Scanning electron microscopic image with EDAX of (a) lead, complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound**



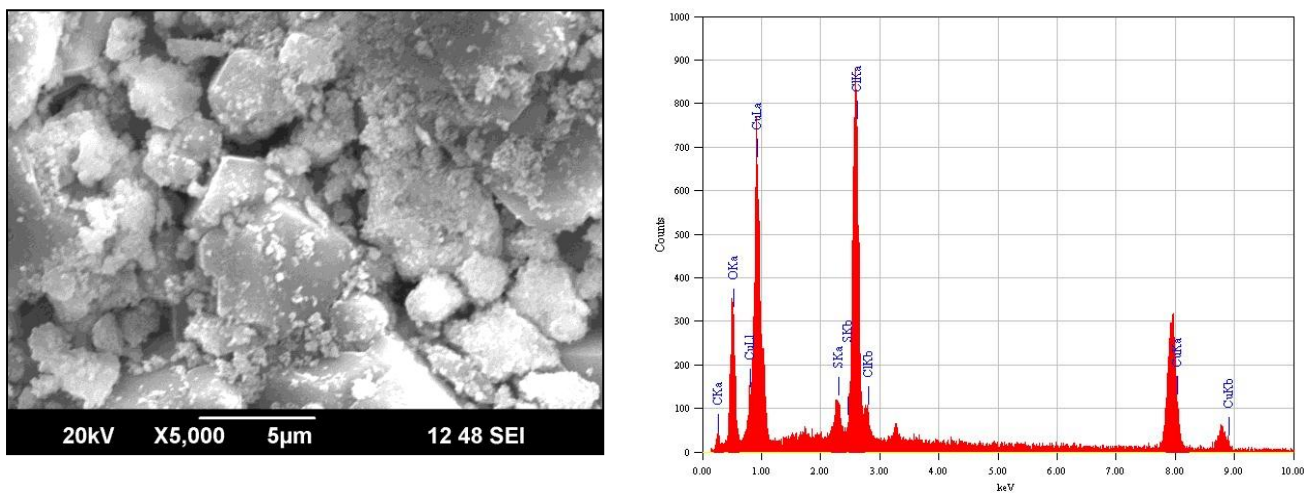
(b)

**Figure-7: Scanning electron microscopic image with EDAX of (b) Zinc, complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-NaphthalenedisulfonicAcid Hexasodium Compound**



(c)

**Figure-8: Scanning electron microscopic image with EDAX of (c) Nickel complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1,3,5-Triazin-2-Yl] amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2,7-NaphthalenedisulfonicAcid Hexasodium Compound**



(d)

**Figure-9: Scanning electron microscopic image with EDAX of (d) copper complex of 4-Amino-3,6-Bis[[4-[[4-Chloro-6-[(3-Sulfohenyl)Amino]-1,3,5-Triazin-2-Yl] Amino]-2-Sulfohenyl]Azo]-5-Hydroxy-2,7-Naphthalenedisulfonic Acid Hexasodium Compound**

#### 4. Conclusions

In the present investigation, the crystal growth of marine dye namely 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfohenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfohenyl]azo]-5-hydroxy-2,7-naphthalene disulfonic acid hexasodium dye compound was successfully carried out under standard laboratory conditions. The grown dye crystals were investigated by sophisticated analytical techniques such as x-ray diffraction and scanning electron microscopy. The results reveal the successful formation of crystals of this organic dye. Since the crystallization of this dye could culminate in good complex formation with transition metals, this part of the work was attempted and successfully implemented.

The dye was made to form complex with the transition elements such as Ni, Cu, Pb and Zn in order to study about their complexing ability degradation behaviour. The complex formed by the dye 4-amino-3,6-bis[[4-[[4-chloro-6-[(3-sulfohenyl)amino]-1,3,5-triazin-2-yl]amino]-2-sulfohenyl]azo]-



5-hydroxy-2,7-naphthalene disulfonic acid hexasodium compound with Ni, Cu, Pb and Zn metals are shows the formation of a coordination complex with a tetrahedral geometry. The FTIR spectrum shows the successful incorporation of Ni metal inside the tetrahedral sites and the same has been amply supported by the x-ray diffraction studies also. The UV-Vis spectrum obtained for this complex demonstrates its strong degradation behaviour besides proves the formation of stoichiometric complex. The elemental analysis of the complex was analyzed through CHNS analysis. The morphology and composition of the complex was evaluated by SEM technique which very well proves the smooth morphology of the crystal. The percentage composition of the dye and the metal was also found to be in definite stoichiometry as evident from the EDAX measurements.

#### ACKNOWLEDGMENT

The authors are thankful to Mahendra Engineering College and AMET University to do the present work and also very thankful to sophisticated test and instrumentation centre **STIC**, Cochin University, Kerala for providing to utilize research lab for all the analysis.

#### References

1. Welham A., (2000) the theory of dyeing (and the secret of life). *J. Soc. Dyers Colour.*, 116:140-143.
2. Hankare PP, Chavan SS. Studies on some binuclear metal complexes with tetradentate ligand derived from 5-(2-thiazolylazo)salicylaldehyde and 2-aminophenol. *Synthesis and Reactivity in Inorganic Metal-Organic Chemistry* 2003; 33(3):423–34.
3. Omar MM, Mohamed GG. Potentiometric, spectroscopic and thermal studies on the metal chelates of 1-(2-thiazolylazo)-2-naphthalenol. *Spectrochimica Acta Part A* 2005; 61(5):929–36.
4. Pandey G, Narang KK. Synthesis, characterization, spectral studies, and antifungal activity of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes with monosodium 4-(2-

- pyridylazo)resorcinol. *Synthesis and Reactivity in Inorganic Metal-Organic Chemistry* 2004;34(2):291–311.
5. Roy R, Chattopadhyay P, Sinha C, Chattopadhyay S. Synthesis, spectral and electrochemical studies of arylazopyridine complexes of palladium(II) with dioxolenes. *Polyhedron* 1996; 15(19):3361–9.
  6. Zaki ZM. Spectral, thermal and electrical properties of some new azo complexes. *Spectrochimica Acta A* 2000;56(10):1917–23.
  7. Mohamed GG, Zayed MA, El-Gamel NEA. Thermal and kinetic studies on solid complexes of 2-(2-benzimidazolylazo)-4-acetamidophenol with some transition metals. *Spectrochimica Acta A* 2002; 58(14):3167–78.
  8. Rageh NM. Electronic spectra, solvatochromic behavior and acid-base properties of some azo cinnoline compounds. *Spectrochimica Acta A* 2004; 60 (1–2):103–9.
  9. Naskar S, Biswas S, Mishra D, Adhikary B, Falvello LR, Soler T, et al. Studies on the relative stabilities of Mn(II) and Mn(III) in complexes with N4O2 donor environments: crystal structures of [Mn(pybzhz)(2)] and [Mn(Ophsal) (imzH)(2)]ClO4 (pybzhz<sup>1/4</sup>N-(benzoyl)-N0-(picolinylidene) hydrazine, Ophsal <sup>1/4</sup>N, N0-o-phenylenebis(salicylideneimine), imzH<sup>1/4</sup>imidazole). *Inorganica Chimica Acta* 2004; 357(14):4257–64.
  10. Gup R, Kirkan B. Synthesis and spectroscopic studies of copper (II) and nickel ( II) complexes containing hydrazonic ligands and heterocyclic coligand. *Spectrochimica Acta A* 2005; 62(4-5):1188–95.
  11. Kandaz M, Yilmaz I, Keskin S, Koca A. Synthesis, spectroscopy and redox properties of a novel (E–E) vic-dioxime and its mono-, di- and trinuclear complexes bearing an 18-membered N2O2S2 macrocyle. *Polyhedron*2002; 21(8):825–34.
  12. H. Kelker, R. Hatz, Hanhbook of Liquid Crystals, Verlag, Chemie, Weinheim, 1980.

13. Anil Kumar, Acoustic letters., 13 (12), 226 (1990).

14. Krishnamurthy T., and Subha L., Rao, Indian J. Pure and Appl. Phy., 247 (1968).

15. Wang J., Stripping Analysis, Principles, Instrumentation and Applications, VCH, Deerfield Beach, 1985.