

SYNTHESIS, SPECTRAL CHARACTERIZATION AND SOLVOTHERMAL DECOMPOSITION, OF BIS(N,N-DIPROPYLDITHIOCARBAMATO) COPPER(II)

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1. Introduction

The chemistry of sulphur containing compounds is exploited in industries, technology and biology. Dithiocarbamates are a class of versatile binding agents, which coordinate with transition, main group, lanthanide and actinide elements predominantly in a bidentate mode [1-5]. Dithiocarbamates find extensive applications in the field of medicine such as in the treatment of bacterial and fungal infections, AIDS, and most recently in the treatment of cancer. Their anti-tumor effects can in part be attributed to their ability to complex tumor cellular copper, leading to binding to and inhibition of the proteasome and in turn initiating tumor cell-specific apoptosis [6, 7]. Dithiocarbamate is also that it can coordinate to the metal ion as a tridentate ligand [8]. Dithiocarbamates as ligands have unique characteristics of stabilizing both low and high oxidation states of transition metal ions [9]. Metal dithiolates are used as single source precursors for metal sulphides. Various iron, cobalt and nickel 1, 1 dithiolates have been investigated as precursors in metal organic chemical vapour deposition [11]. Earlier studies have shown that the bis (N, N'dialkyldithiocarbamato) copper (II) complexes with general formula $[Cu(S_2CNR_2)_2]$ have distorted square planar geometry [12, 13, 14]. Recent publications established that copper (II) dithiocarmates are useful precursors to CuS nanoparticles [15,16]. In this paper, we report the synthesis, spectral, thermal decomposition of $Cu(dtc)_2$ are reported. Copper(II) di-thiocarbamates were used as precursors for the preparation of CuS nano particles by a non conventional solvothermal method. The CuS nano particles were characterized by powder XRD, SEM and EDX.

2. Experimental

All reagents and solvents were commercially available analytical grade materials and were used as supplied. Dipropylamine was supplied by Sigma Aldrich. IR spectra were recorded on an ABB Bomem MB 104 spectrometer (4000–500cm) as KBR pellets. Scanning electron micrographs of the samples were recorded with JOEL JSM-5610Lv microscopes. Cyclic voltammetric studies were carried out using a CH1604C electro chemical analyzer. Glassy carbon was used, as working electrode and the counter electrode was a platinum wire. The reference electrode was Ag/AgCl. Tetrabutylammonium per-chlorate (0.01 M) was used as the supporting electrolyte. The experiments were carried out under oxygen free atmosphere by bubbling purified nitrogen gas through the solution at room temperature. Thermal analysis was carried out on a STA 409 PC thermal science instruments. The diffraction intensities were collected in the 2 θ range (2–80°) using Bruker-D8 X-ray diffractometer equipped with Mo K α radiation at fixed current and potential.

3. Preparation

Preparation of Bis(dipropyldithiocarbamto)copper(II); [Cu(dpdtc)₂]

The compound [Cu(dpdtc)₂] was prepared by mixing diphenylamine (4 mmol, 0.54 mL) and carbon disulphide (4 mmol, 0.24 mL) in ethanol under ice cold condition (5°C). To the yellow dithiocarbamic acid solution, aqueous solution of CuSO₄.5H₂O (2 mmol, 0.500 g) was added with constant stirring. A brown solid separated from the solution, which was filtered, washed with alcohol and was then dried in air. Preparation of CuS nano particles by non-conventional solvothermal decomposition. A mixture of bis (dipropyl dithiocarbamto)copper(II) (1.0 g) as a clear solution in chloroform (100mL) was heated with diethylenetriamine (2mL) at 60 °C for 45 min. Solid black copper sulfide obtained was separated from chloroform, washed with ether, chloroform and dried in air. Qualitatively, the ease of formation of nano sulfide is measured as the time of first appearance of the sulfide on decomposition, (yield 95%, dec., 230°C). Anal. Calc. for C₁₄H₂₈N₂CuS₄ : C, 40.40; H, 6.78; N, 6.73. Found: C, 40.17; H, 6.79; N, 6.98

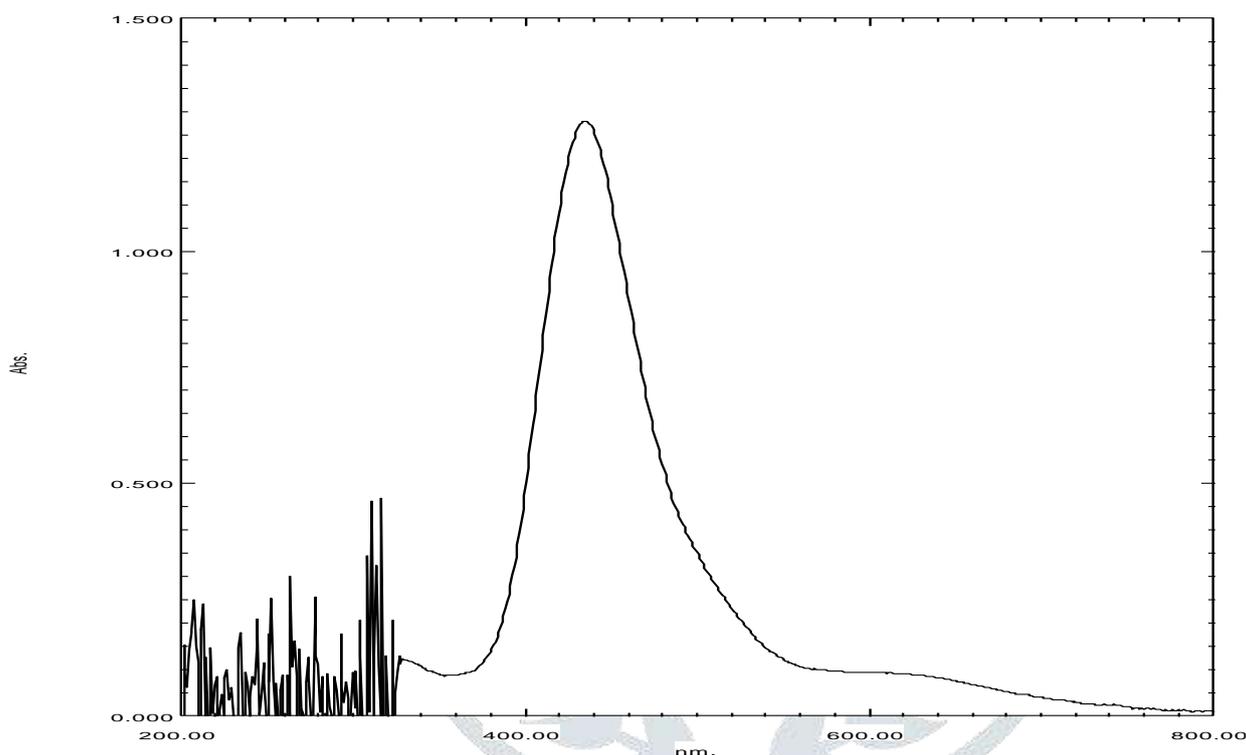
4. RESULT AND DISCUSSION

4.1 Electronic spectra

Electronic spectrum of the [(Cu(dpdtc)₂] are shown in fig 1. In the Cu(II) complex, the bands observed below 350 nm are due to intraligand π - π^* transitions, mainly associated with the N-C=S and S-C=S groups. Several authors ascribe intense bands in the 350–425 nm regions to either metal-ligand or

ligand-metal charge transfers in compounds [17]. In addition to the charge transfer bands, bands observed in the range 425–650 nm are due to d–d transitions [18]. In the parent complex, the band at 435nm (λ max 20833; ϵ : 1125 l mol⁻¹ cm⁻¹) is due to $dz_2 \rightarrow dx_2-y_2$ transition and the one at 612 nm (λ max 15898; ϵ : 375 l mol⁻¹ cm⁻¹) is due to $dxy \rightarrow dx_2-y_2$ transition. In Cu(II) complex, the charge transfer bands are observed below 400 nm. Electronic spectral data for the complex support the assumption of square planar geometry around the divalent copper in the complex.

Fig.1. Electronic spectra of the complex [Cu(dpdtc)2]



4.2. IR spectral studies

IR spectrum of the compound is shown in fig. 2. The spectra shows two characteristic bands due to ν C-N and ν C-S vibrational modes. For complex ν (C–N) thioureide bands are observed at, 1503, and 1507 cm⁻¹. The ν (C–S) stretching bands are observed around 1100 cm⁻¹ without any splitting, supporting the bidentate coordination of the di-thiocarbamate moiety. The ν C–S bands are observed around 1000 cm⁻¹ without any splitting, supporting the bidentate coordination of the dithiocarbamate moiety [19, 20]. In all the complexes, the aliphatic ν C–H stretching vibrations appeared around 2900 cm⁻¹.

The $\nu_{\text{C-N}}$ single bond vibration appeared in the region: 1240-1245 cm^{-1} in all the complexes [21].

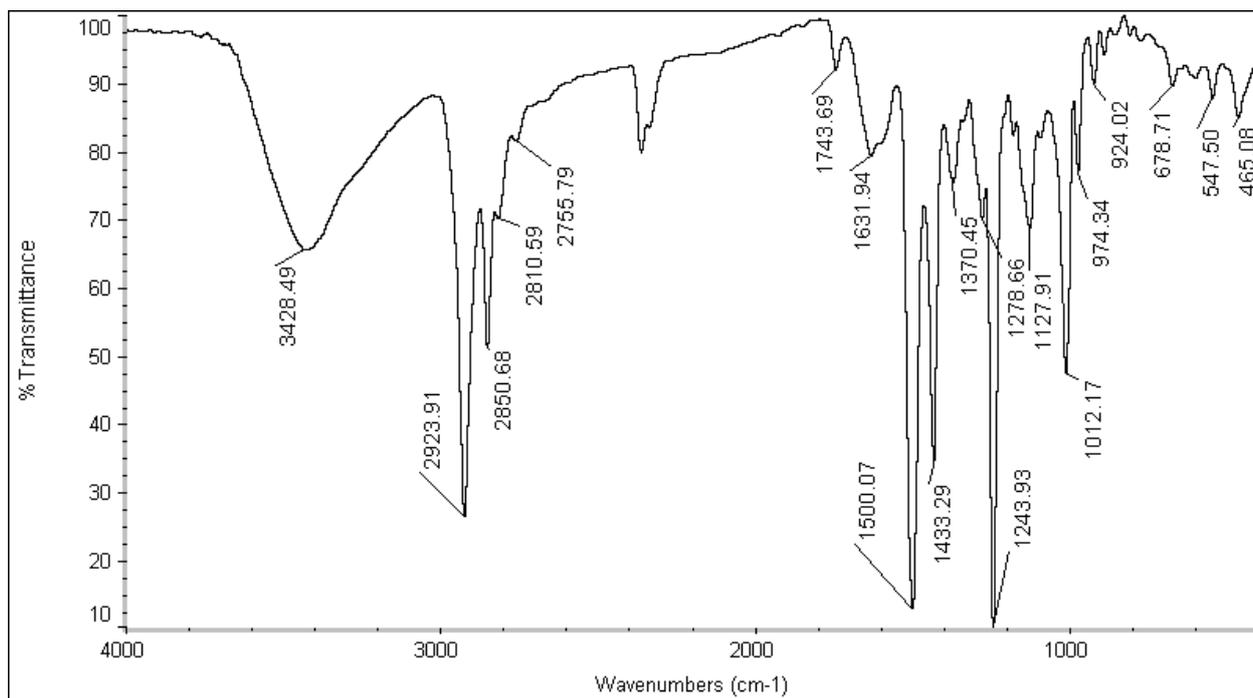


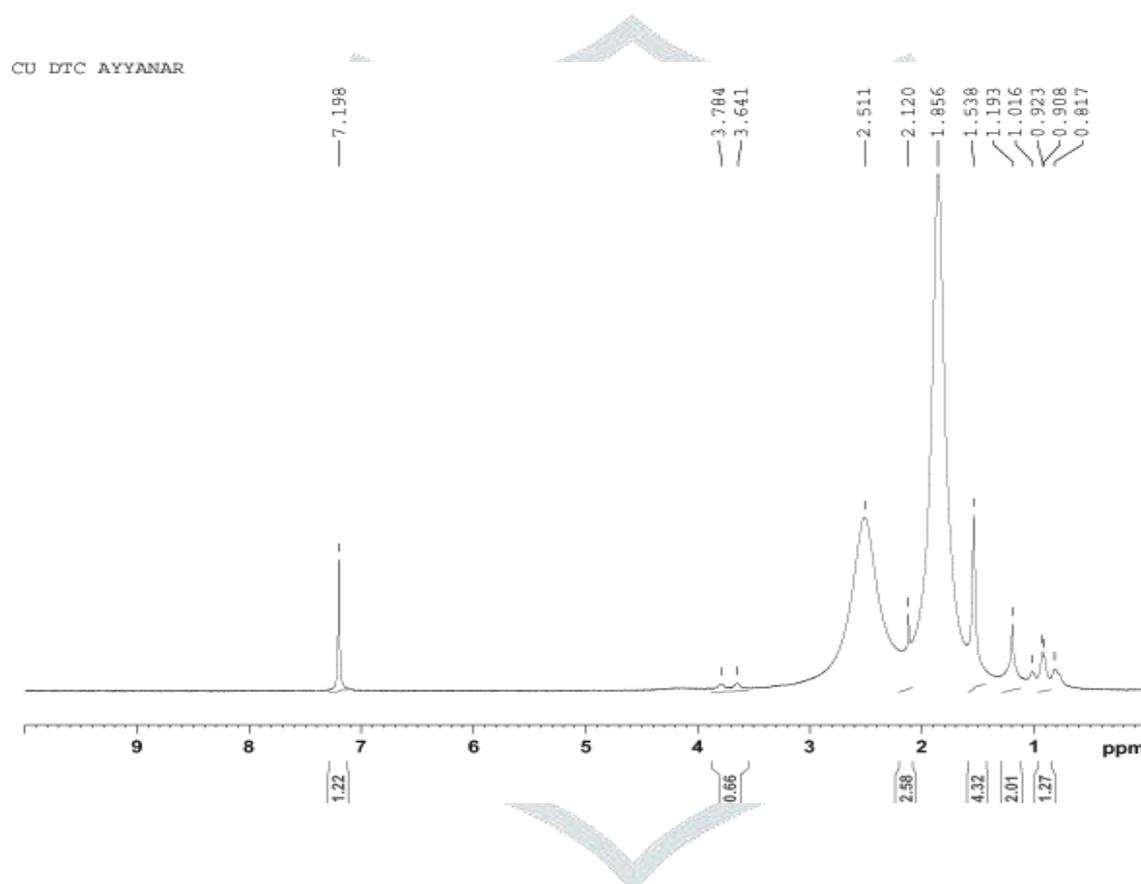
Fig.2 IR spectra of $[\text{Cu}(\text{dpdtc})_2]$

4.3. Nuclear magnetic resonance spectra

^1H NMR Spectra for the complex are shown in Fig 3. In the complex α – and β -methylene protons of dipropyl are equivalent due to the presence of symmetry in the coordination environment. In the table 1, only the region in which all the above proton signals observed are given and no individual splitting pattern is discussed. In this parent compound, the dipropyl group is equivalent and hence individual splitting pattern for α , β - and γ - methylene protons are not indicated in the table. The observed deshielding of the $-\text{CH}_2$ protons in the compound is attributed to the shift of electron density on the sulfur (or the metal) through the thioureide π system [22]. In these parent compound complex the α methylene, protons adjacent to nitrogen atom undergo strong deshielding and appear around 3.0 ppm.[23]. The chemical shift of the compound is appeared as a broad signal indicates the compound is paramagnetic. Due to non-availability of the guoy balance, magnetic susceptibility could not be measured. But NMR spectrum of the copper (II) dithiocarbamate complex clearly indicated the compound is paramagnetic. Hence central metal atom copper present in copper dithiocarbamate complex $[(\text{Cu}(\text{dpdtc})_2)]$ must be Cu(II).

Table 1. ^1H NMR spectral data of the complexes (Chemical shifts in ppm)

Compound [Cu(dpdtc) ₂]	Dipropyl group			
	α -CH	β -CH ₂	δ -CH ₂	δ -CH ₂
	3.0	1.64-2.5 (Collapsed multiplet)		

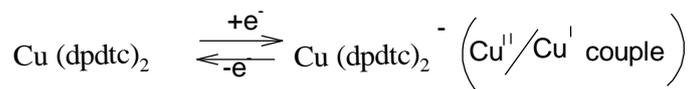
Fig.3 ^1H NMR Spectra of [(Cu(dpdtc)₂)]

4.4. ^{13}C NMR spectra

In the dipropyl group, α -CH₂, β -CH₂, γ -CH₂ splitting is not clear. Hence, the non-clearness of splitting in dipropyl group indicates the compound must be paramagnetic. In side chain, the α -, β -, γ - methylene carbons appear to be deshielded largely and but no splitting are observed in the downfield region for the parent complex due to paramagnetic nature of the complex [Cu(dpdtc)₂].

4.5. Cyclic voltammetry

Cyclic voltammograms of the complex are recorded in CH_2Cl_2 and TBAB was used as supporting electrolyte. Representative cyclic voltammograms are given in **Fig.4**. The copper dithiocarbamate complex show one electron reduction, which are quasi-reversible due to the Cu(II)/Cu(I) redox process as given below.



The redox potentials for the complex (scan rate: 100 mVs^{-1}) are given in **Table.2**. High responding currents and smaller peak potential separation indicates a greater reversibility as well as stabilization of Cu(II) complexes species. The neutral copper (II) complex show large reversible reduction potentials (-1010 mV) in keeping with their reluctance to add electron density to already electron rich metal centers of the complex. A higher reduction potential of the complex indicates the effect of the presence of electron releasing methyl group in the complex. The reduced form of the complex show their readiness to lose electron density as indicated by the higher second reversible oxidation potential values (-640 mV). Therefore the neutral copper dithiocarbamate complexes display one quasi-reversible one electron reduction process (ΔE , mV) : (370) which is assigned to be $\text{Cu(II)} - \text{Cu(I)}$ couple. The high negative potential ($< -1.0 \text{ V}$) of copper (II) – copper (I) reduction process can account for the preferential stabilization of copper in +2 oxidation state in the copperdithiocarbamate complex under atmospheric conditions. The electrochemically generated copper(I) complex $[\text{Cu(L}_2)]^+$ have been found to be quite unstable and spontaneously oxidize to the parent $[\text{Cu(L}_3)]$ state which has essentially precluded the isolation of the corresponding copper(II) analogue [24,25].

Table:2 Reduction potentials (mV) for the complexes $[\text{Cu(dpdte)}]_2$

Compound	E_p (mV)		
	E_p^c	E_p^a	ΔE_p (mV)
$[\text{Cu(dpdte)}_2]$ (2)	-1010	-640	370

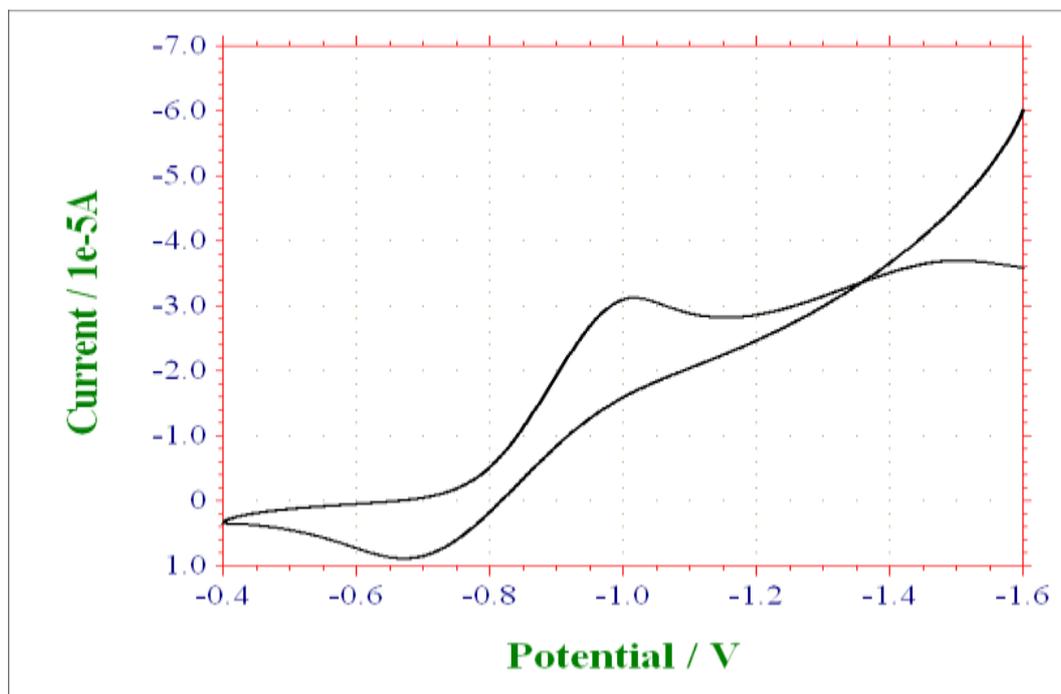


Fig.4 Cyclic voltammograms of [Cu (dpdtc)₂]

4.6. Thermogravimetry

The complex are subjected to TG study. Thermogram of the complex are shown in fig.5 and thermogravimetric data are given in table 3. Initially, water molecule is lost around 256°C in an endothermic process for the parent complex [Cu(dpdtc)₂] \cdot H₂O (exptl.:94.0 %, calcd.96.0 %). The second stage of thermal decomposition starts around 322°C corresponding to the formation of Cu(NCS)₂ (exptl.: 36.5 %, calcd. 36.0 %). Subsequently, above 632°C Cu(NCS)₂ decays thermally in an endothermic process to stabilize as CuS. Final residue obtained is CuS (exptl.: 18.7 %, calcd. 19.1 %). The results of TG analysis agreed well with the proposed formula of the complex[26]. Pxd of the residue could not be carried out due to paucity of the residue. Controlled synthesis of CuS nanoparticles by the solvothermal decomposition of a single source precursor; [Cu(dpdtc)₂] (1 g) as a clear solution in chloroform (100mL) was heated with diethylenetriamine (2 mL) at 80°C. The black nano CuS was obtained as a suspension. The precipitate was filtered and washed with ether, chloroform and the nanoparticles were collected and dried.

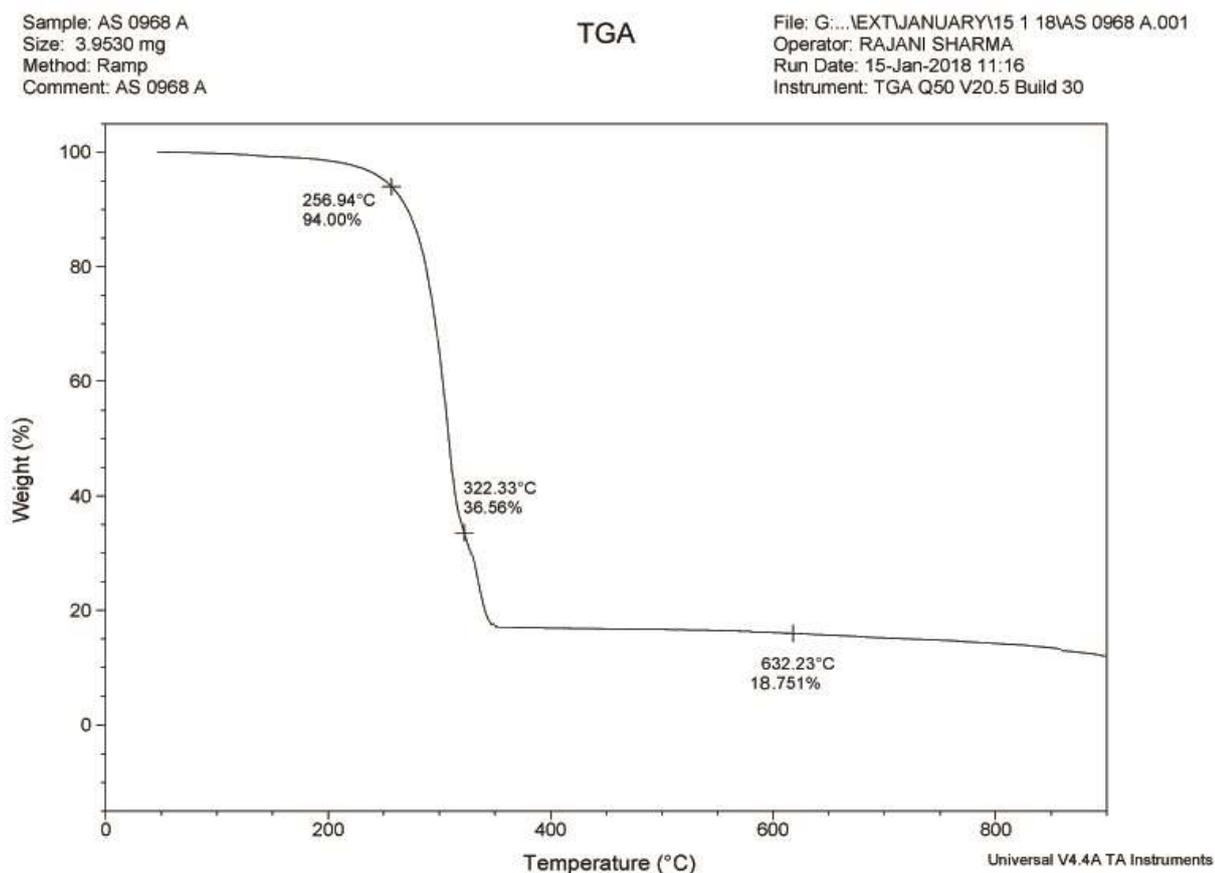
Fig.5 Thermogram of $[\text{Cu}(\text{dpdtc})_2] \cdot \text{H}_2\text{O}$

Table.3 Thermo gravimetric data

Complex	MW	Mass loss		Decomp. range	Fragment lost/ end product
		exptl.	calcd.		
$[\text{Cu}(\text{dpdtc})_2] \cdot \text{H}_2\text{O}$	498.2	94.0	96.0	256°C	$-\text{H}_2\text{O}$
		36.5	36.0	361°C	$\text{Cu}(\text{NCS})_2^*$
		18.7	19.1	>600°C	CuS^*

*Proposed based on final mass left out.

4.7 Controlled synthesis of CuS nano particles by the solvothermal decomposition of a single source precursor; $[\text{Cu}(\text{dpdtc})_2]$

$[\text{Cu}(\text{dpdtc})_2]$ (1 g) as a clear solution in chloroform(100mL) was heated with diethylenetriamine (2 mL) at 80°C. The black nano CuS was obtained as a suspension. The precipitate was filtered and washed with ether, chloroform and the nanoparticles were collected and dried.

SEM-EDX analysis

Fig.6 is a scanning electron micrograph of CuS nanoparticles and Fig.7 show a typical EDX pattern of CuS particles. The particles are crystalline in nature. The micrographs clearly indicate the spherical morphology of the particles formed. The particles are agglomerates and appeared as cluster. The elemental composition of CoS nanoparticles is determined using SEM-energy dispersive analytical X- ray (EDX) spectroscopy by performing the spot measurements on particles. The major peaks are due to the presence of Cu along with sulphur. The elemental ratio of Co to S in the CS nanoparticles is 80:20

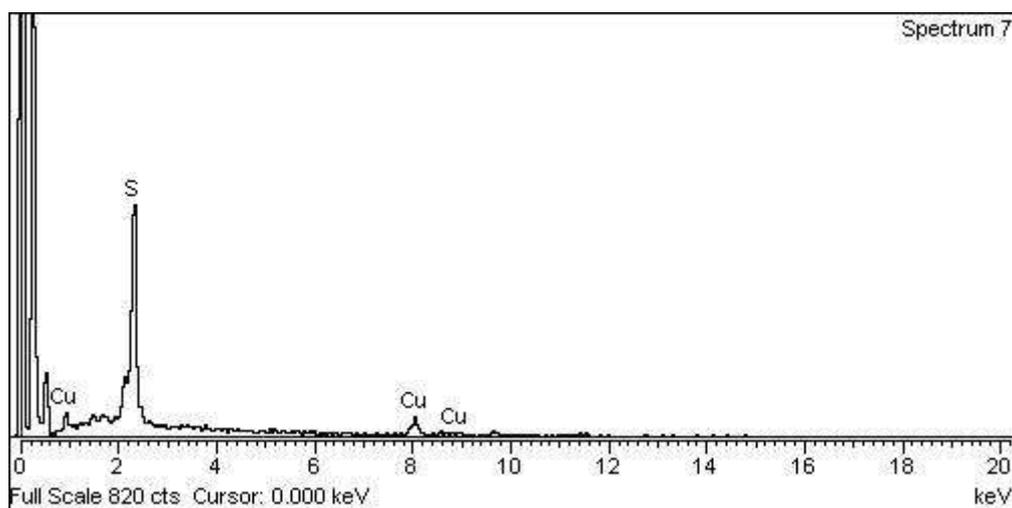


Fig. 6 The EDX spectra of nano CuS particles

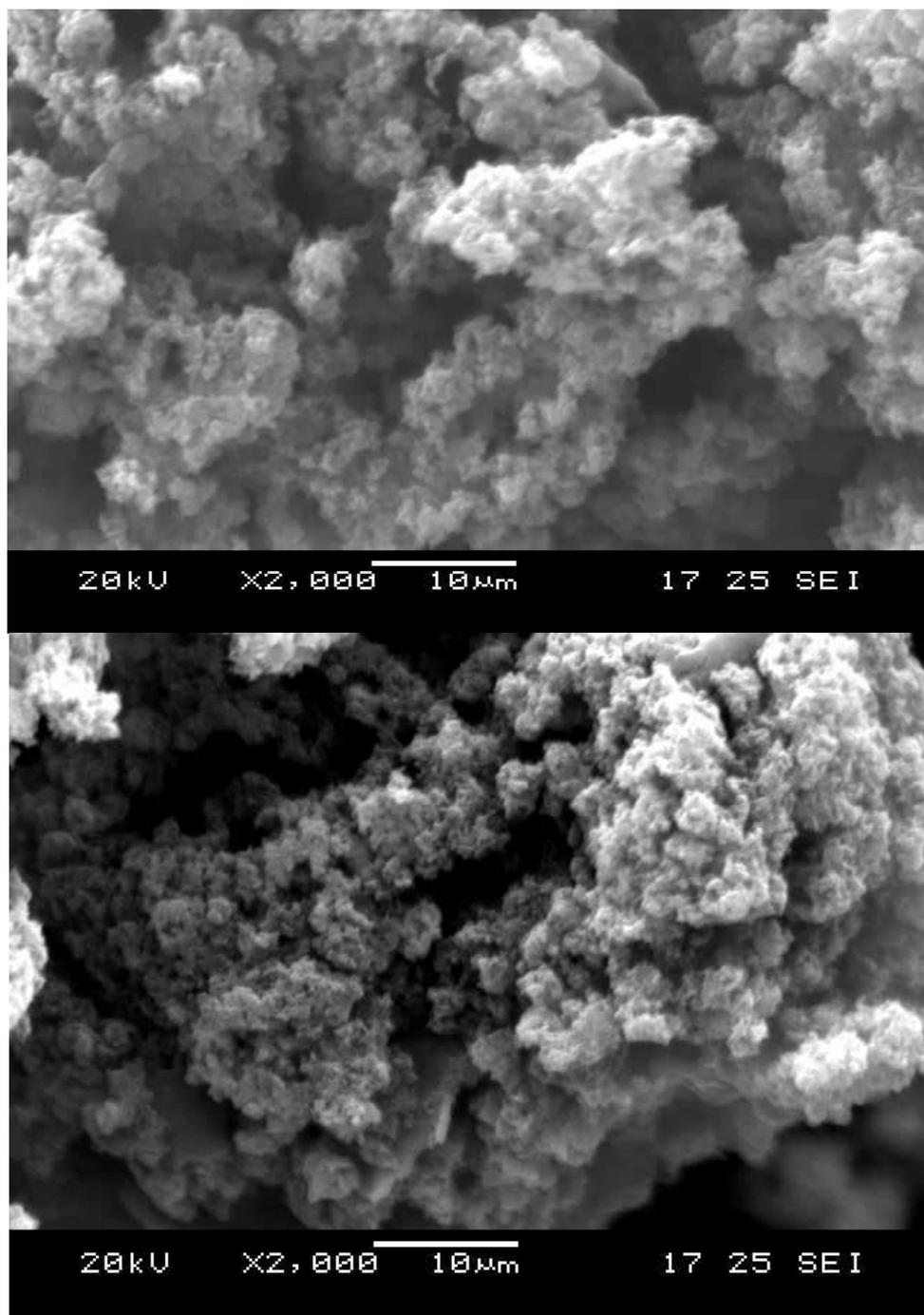
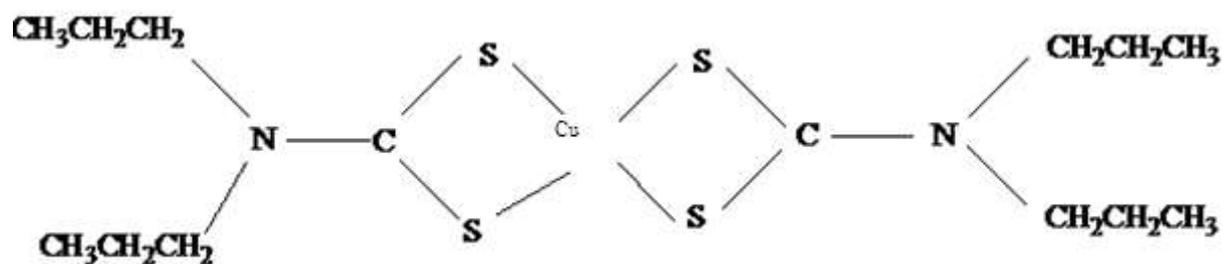


Fig. 7 SEM images of nano Cu

Proposed structure of the compound



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