synthesis, spectral characterization of nickel(II) dithiocarbamates and its solvothermal decomposition to nano nickel (II) sulphide

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ABSTRACT

The planar nickel(II) dithiocarbamate [Ni(dpdtc)$_2$] (where dpdtc=dipropyldithiocarbamate) have been prepared, characterized by elemental analysis, electronic, infrared, NMR('H, ^{13}C) spectra. Electronic spectra of complex showed bands at 479 nm (λ max 20833; ϵ: 1125 l mol^{-1} cm^{-1}) is due to $d_z{}^2 \rightarrow d_x{}^2{}_{-y}{}^2$ transition and the one at 629 nm (λ max 15898; ϵ: 375 l mol^{-1} cm$^{-1)}$ is due to dxy → dx^2-y^2 transition. The characteristic thiouride band appeared at 1485 cm^{-1} for the nickel complex. NMR spectra of the complexes show the (N)^{13}CS^2 -chemical shifts at 206 8 indicate the nickel dithiocarbamate complex are diamagnetic and planar. CV studies indicate that the complex undergo one electron reduction process. Themogravimetric study of the nickel(II) dithiocarbamate complex clearly supported the proposed formulae of the complex. Solvothermal decomposition of the nickel(II) dithiocarbamate complex was carried out for the synthesis of nanoparticals. Information on the size and morphology of the product have been confirmed on the basis of SEM and EDX analysis.

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1. Introduction

Investigations on the metal ion - sulphur containing ligand systems have relevance to biological and analytical aspects of chemistry including general academic interest. A major class of sulphur containing ligands is obtained by the general reaction of carbon disulphide with various nucleophiles. Major types of ligands which have been obtained, with exciting coordination properties are dithiocarbamates[1]. The dithiocarbamates as ligands form numerous complexes with almost all the transition metal ions and main group elements.

There is a great deal of interest associated with their complexes [2]. Dithiocarbamates as ligands have unique characteristics of stabilizing both low and high oxidation states of transition metal ions [3]. The contribution of resonance form to the structure of the dithiocarbamate ligands and complexes was offered as an explanation for the antifungal activities of these compounds [4]. Several reports have appeared in the literature dealing with the properties, reactivities, geometries and wide variety of applications, in medicine [5], in agriculture [6], in the rubber industry [7]. Various dithiocarbamates are useful in the trace metal determination in food [8], in the pharmaceutical products, in biological samples [9], and in general as an analytical reagent [10]. Some of the publications on the complexation of dithiocarbamates with metal oxides [11], metal powders [12], and metal rods or foils [13] instead of the corresponding metal salts indicate the coordinating ability of the ligands. Various dithiocarbamate ligands with polar substituents have also been investigated as therapeutic agents in cases of heavy metal toxicity [14] and AIDS [15]. 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[16]. The variety of dithiocarbamates bis (N-alkyldithiocarbamato) nickel(II) complexes, $[Ni(S_2CNH(n\text{-}pr)_2]$, $[Ni(S_2CNH(ipr^{’})_2][17]$, $[Zn(S_2CN(C_2H_5)_2]_2[18]$, $M[(S_2CN(C_2H_5)_2)]_2$ (M=Pb,Cd)[19], $Pb[(S_2CN(Bu_2^{”})_2][20]$, $Cr[(S_2CN(C_2H_5)_2)]_3[21]$ and $Cu[(S_2CN(Pr_2)_2][22]$ have been used as single source precursors for the production of thin layers of metal sulphides, viz., NiS,ZnS,PbS,CdS,Cr_2S_3 and Cu_2S respectively by chemical vapour deposition method. In this paper we report the synthesis , spectral characterization and solvothermal decomposition of single source precursor.

2. Experimental

All the reagents and solvents employed were commercially available analytical grade materials and were used as supplied without further purification. IR spectra were recorded on an Avatar Nicolet FT-IR spectrometer [range 4000–400 cm^{-1}] as KBr pellets of the compounds. Electronic spectra of the complex recorded in CH_2Cl_2 on a Hitachi U-2001 double beam spectrometer. ^1H, and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer at room temperature using $CDCl_3$ as the solvent. Cyclic voltammetric studies were carried out using a CH1604C electrochemical analyzer. Glassy carbon was used as working electrode and the counter electrode was a platinum wire. The reference electrode was Ag/AgCl. Tetrabutylammonium perchlorate (0.01 M) was used as the supporting electrolyte. The experiments were carried out under oxygen free atmosphereby bubbling purified nitrogen gas through the solution at room temperature. Thermal analysis was carried out on an STA 409 PC thermal science instruments. Powder X-ray diffraction intensities were collected in the 2θ range 2 -80· using Bruker-D8 X-ray diffractometer equipped with Cu-K a radiation at fixed current and potential. The scan speed and step size were 0.05 ? min? 1 and 0.00657 respectively.

3. PREPARATION OF THE COMPLEX'

3.1 Preparation of bis(N-N-dipropyldithiocarbamato)nickel(II); [Ni(dpdtc)$_2$**]**

N,N–diphenylamine(0. 27mL, 2mmol) and carbon disulphide (~0. 076 mL in excess, 1mmol) in ethanol (20mL) were mixed under ice-cold condition (5°C) to form yellow solution of the corresponding diphenylaminedithiocarbamic acid. To the dithiocarbamic acid solution, an aqueous solution of nickel chloride hexahydrate (240 mg, 1mmol) was added with constant stirring. A pale green precipitate separated, which was filtered, washed with water and ethanol. The solid was then dried over anhydrous calcium chloride. (Yield : 95% ; dec. : 220-222°C).($C_{14}H_{28}N_2S_4Ni$) (411.34) (%):C,40.88; H, 6.86; N,6.81 Found (%): C, 40.68; H, 6.98;N, 6.99.

4. Electronic spectra

Electronic spectra of the complex are shown in Fig.1 Electronic spectrum of the parent [Ni(dpdtc)$_2$] shows bands at 479, 571 nm and the In the Ni(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 [23]. In addition to the charge transfer bands, bands observed in the range 425–650 nm are due to d–d transitions [24]. In this parent complex, the band at 479 nm (λ max 20833; ϵ: 1125 l mol^{-1} cm^{-1}) is due to $d_z{}^2 \rightarrow d_x{}^2{}_{-y}{}^2$ transition and the one at 629 nm (λ max 15898; ϵ : 375 l mol^{-1} cm$^{-1)}$ is due to dxy → dx^2-y^2 transition. In Ni(II) complex, the charge transfer bands are observed below 400 nm. Electronic spectral data for the complexes support the assumption of square planar geometry around the divalent nickel in all the complexes

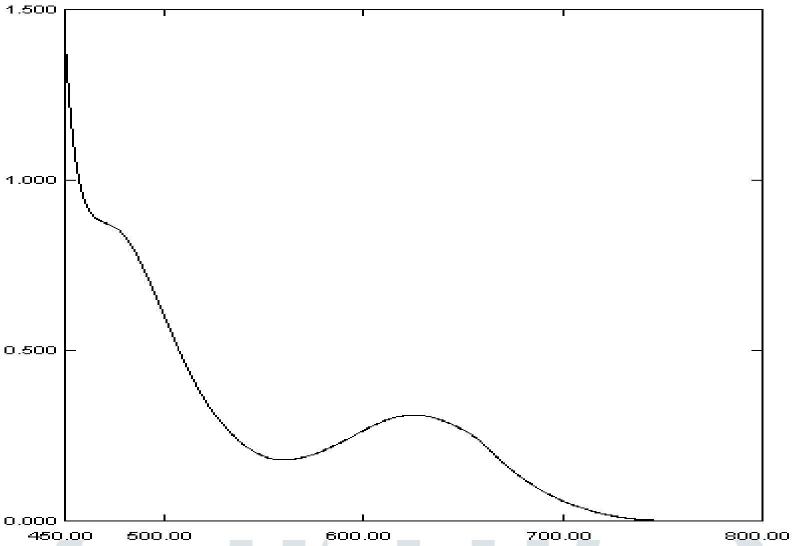


Fig.1 Electronic spectra of the complex [Ni(dpdtc)$_2$]

5. Infrared spectra

Representative infrared spectra of the complex are shown in Fig 2. The spectra show two characteristic bands due to υ_{C-N} and υ_{C-S} vibrational modes. The υ_{C-N} has been used as a measure of the contribution of the thioureide form (c) to the structure of the dithiocarbamate. Energy associated with the C-N stretching in the case of dithiocarbamate ligand lies intermediate between the stretching frequency regions assigned to υ_{C-N} single bond (1250-1350 cm^{-1}) and double bond (1640–1690 cm^{-1}). This is best explained as vibration of polar $C = N^+$ bond [25]. The υ_{C-S} bands are observed around 1000 cm^{-1} without any splitting, supporting the bidentate coordination of the dithiocarbmate moiety [26]. In the complex, the aliphatic υ_{C-H} stretching vibrations appeared around 2960 cm^{-1}. The υ_{C-N} single bond vibration appeared in the region: 1240-1245 cm^{-1} in all the complexes.

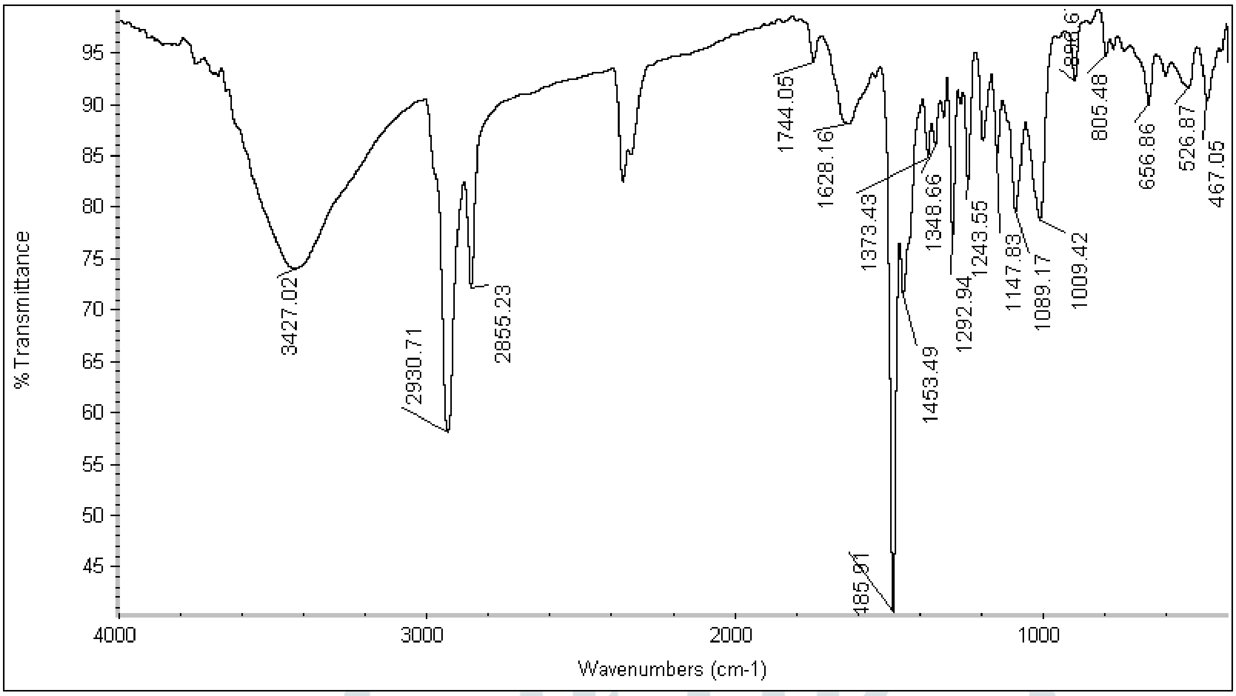


FIG. 2 IR SPECTRA OF THE COMPLEX [Ni(dpdtc)$_2$]

6. Nuclear magnetic resonance spectrum

6.1 ^{1}H NMR spectrum

^{1}H NMR spectra for the complex is shown in Fig.3 and the chemical shifts are given in Table 1. In the complex $\alpha -$ and β- methylene protons of dipropylamine are equivalent due to the presence of symmetry in the coordination environment. In the table only the region in which all the above proton signals observed are given and no individual splitting pattern is discussed. The observed deshielding of the –CH$_2$ protons in all the compounds [27] is attributed to the shift of electron density on the sulfur (or the metal) through the thioureide π system. In the complexes, the $\alpha -$ methylene protons adjacent to nitrogen atom undergo strong deshielding to give signal around 3.4ppm. The β, CH$_2$ - signals are observed at 2.5 ppm and , δ CH$_2$ - signals are observed at 2.1 ppm.

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

	Dipropyldithiocarbamate		
Compound	αCH_3	αCH_2	ύCH_2
[Ni(dpdtc)$_2$]	3.4	2.5	2.1

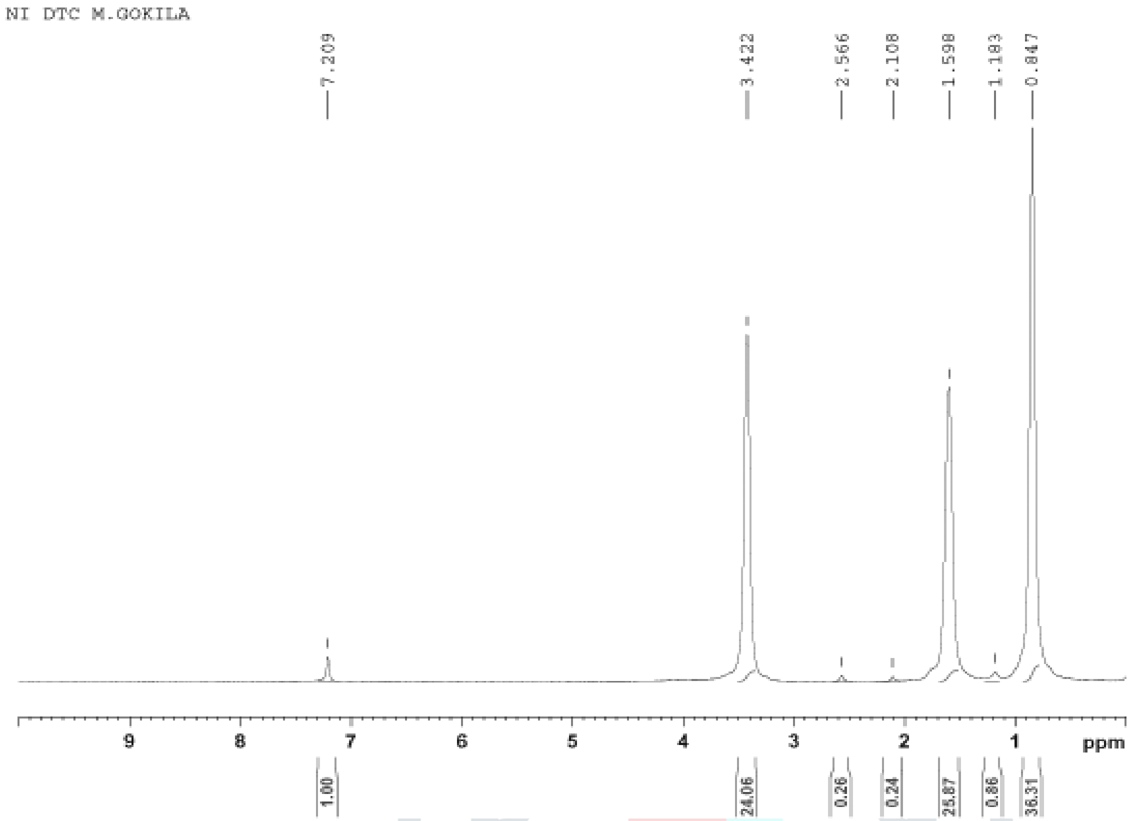


Fig.3.^{1}H NMR spectra of [Ni(dpdtc)$_2$]

6.2 ^{13}C NMR spectra

^{13}C chemical shits of synthesized complex are listed in Table 2. ^{13}C NMR spectra of the complex are shown in Fig. 4**.** The most important chemical shifts of thioureide carbons ($S_2{}^{13}CN$) are observed at 206.8. (c)The mesomeric shift of electron density from dithiocarbamate moiety towards the metal centre contributes to the up field shift from the normal chemical shift of [Ni(dtc)$_2$] complexes (206-210 ppm) [28]. In the complex, α-CH_2 carbon appears to be deshielded to a great extent and the signals are observed at 59.7ppm. The β-CH_2 carbon signals are observed at 29.5 ppm for. The υ-CH_2 carbon signals are observed around 11.1 ppm for complex

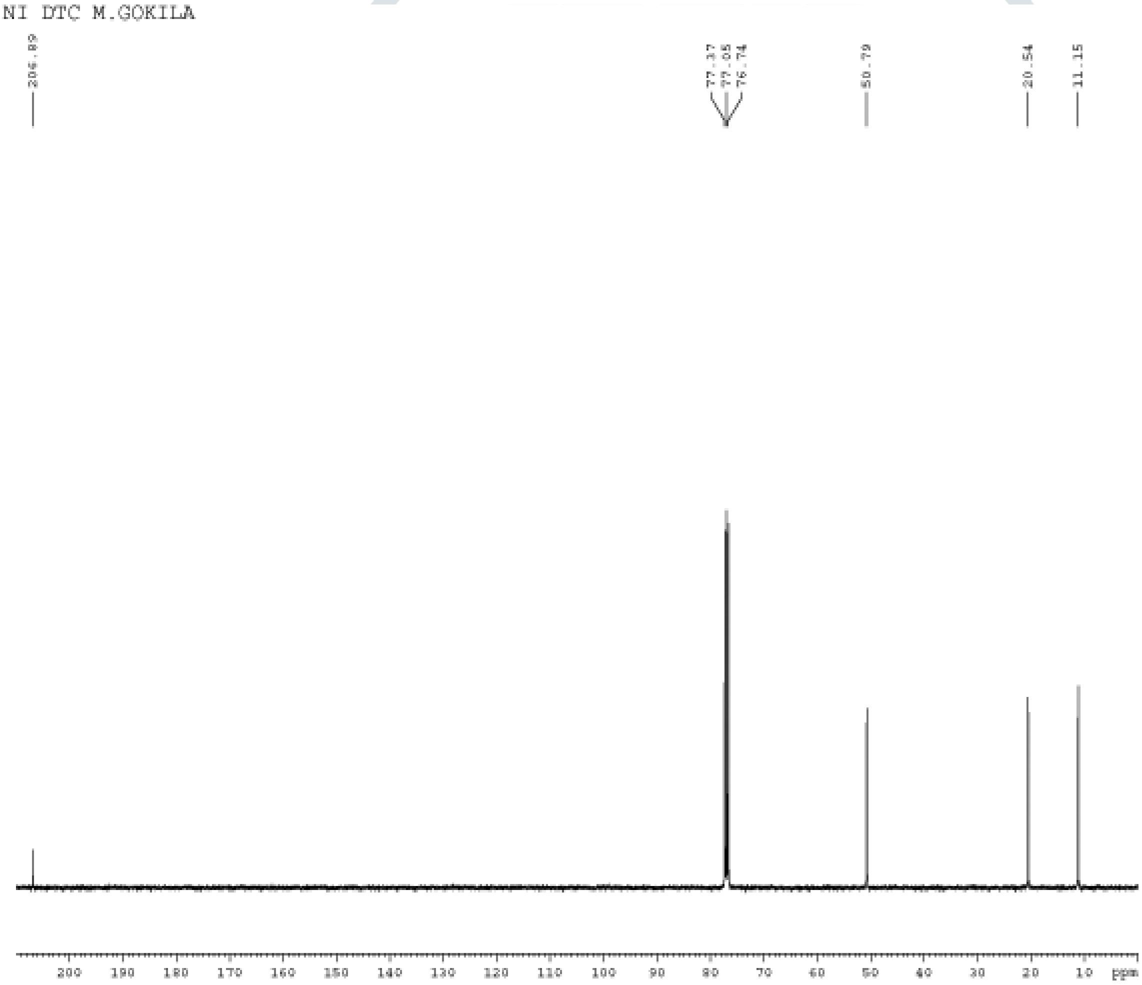


Fig.4 ^{13}CNMR spectra of [Ni(dpdtc)$_2$],

	Propyl group	>N^{13}CS$_2$

Compound				(Thioureide)
	α-CH_2	β CH_2	γ-CH_2	
[Ni(dpdtc)$_2$]	59.7	29.5	11.1	206.8

Table 2. ^{13}C NMR spectral data of the complex (chemical shifts in ppm)

7. Cyclic voltammetry

The representative cyclic voltammograms are given in Fig.5. The reluctance to add more electron density to the already electron rich metal centre is evidenced by the relatively high negative potential of the parent [Ni(dpdtc)$_2$] complex (-1352 V). Based on the previous studies [29] of similar compounds, it is being observed that the reduction process is one electron in nature

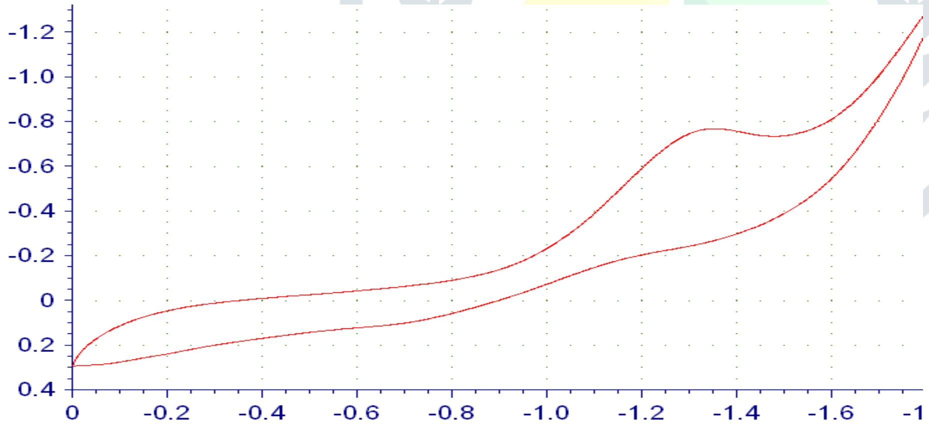


Fig.5. Cyclic voltagram of [Ni(dpdtc)$_2$]

8. Thermogravimetry

The complex are subjected to TG study and the thermograms are shown in Fig. 6 The temperature ranges and percentage mass losses of the decomposition reactions are given in Table 3. From the thermogram of the parent complex [Ni{dpdtc)$_2$]· $2C_2H_5OH{\cdot}H_2O$ it is observed that the complex is thermally stable upto 256˚C. At 256˚C, the compound shows the first sign of thermal decay and lose water molecule {exptl. : 96.82%, calcd. : 96..54%) which continues upto 360˚C and the end products matches in mass with Ni(SCN)(CH3)(exptl. : 21.88%, calcd. : 25.14 %). On further increase in temperature around 740˚C, CH_2-CH=CH_2NCS gets stabilized (exptl. : 19.11 % , calcd. : 19.00 %). At around 900˚C another thermal decay is observed corresponding to the stabilization of NiS(exptl. 17.12 %, calcd. 17.30 %). The experimentally observed values and theoretically calculated values for the mass losses and the end products obtained match well within experimental error. All the thermal decompositions mentioned are exothermic in nature.

Complex	MW	Mass loss		Decomp. Range	Fragment lost/ end product
		exptl.	**calcd.**		
[Ni(dpdtc)$_2$]·2 C_2H_5OH. H_2O	521.2	96.54 25. 8 19.11 17.12	96. 82 21.1 19.00 17.30	256°C 360°C 740°C >900°C	$^{H}{}_2O$ Ni(SCN)(CH_3) CH_2-CH=CH_2 NCS NiS

Table . 3. Thermogravimetric data

*Proposed based on final mass left out.

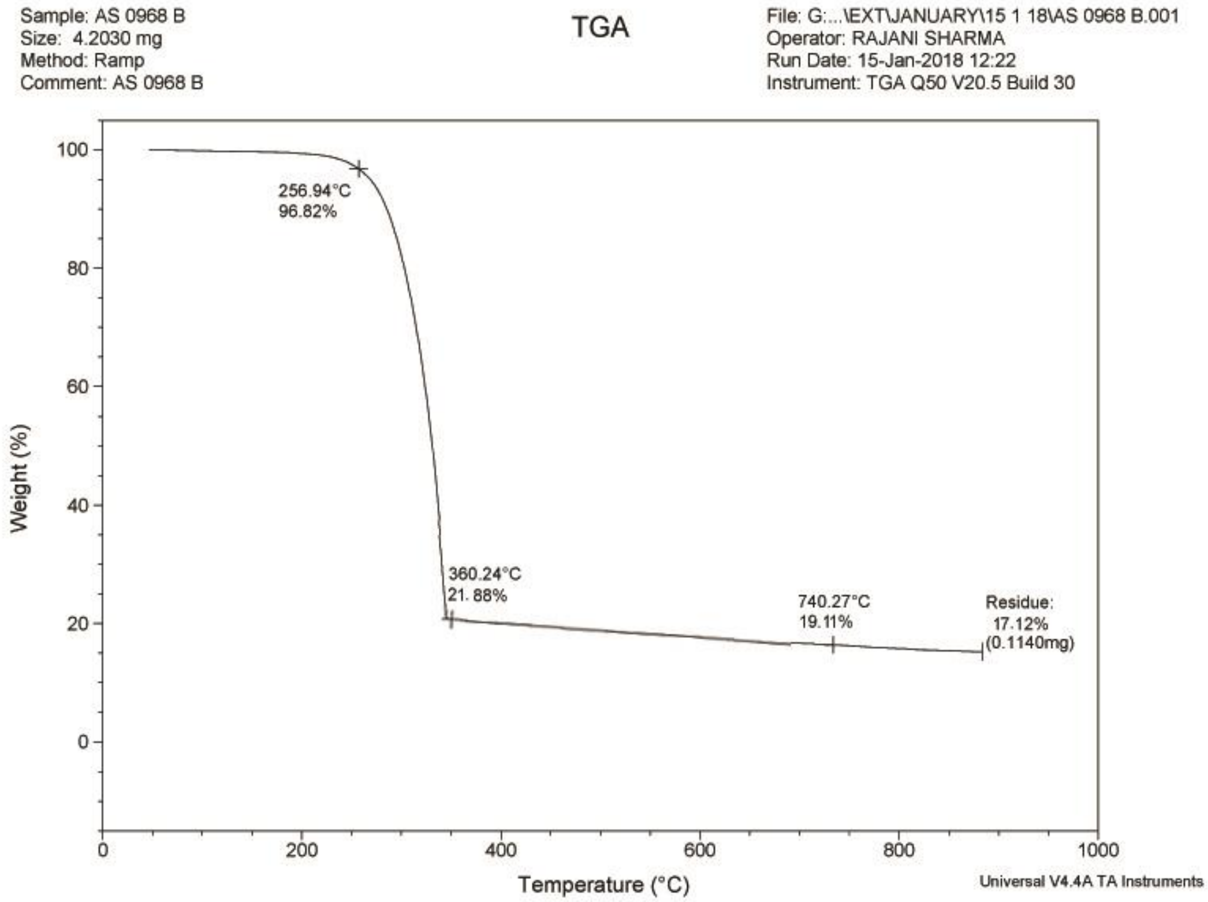


Fig.6. Thermogram of the complex $[Ni(dpdtc)_2]$·

9. SYNTHESIS AND CHARACTERIZATION OF NiS NANO PARTICLES

9.1 Controlled synthesis of NiS nano particles by the solvothermal decomposition of a single source precursor; $[Ni(dpdtc)_2]$

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

9.2 Powder XRD measurements

Powder XRD pattern recorded at room temperature is shown in Fig.7

The strong peaks corresponding to (300), (131) and (110) reflections agree with the JCPDS-pattern (JCPDS file No: 65-3686) (Rhombohedral, space group R3m, a = 9.619, c = 3.149) [30]. Average diameter of the NiS particles are estimated to be 40 nm by Debye – Scherrer calculation from the PXRD pattern [31].

9.3 SEM-EDX analysis

Fig.8 scanning electron micrograph of NiS particles and Fig.9 show a typical EDX pattern of NiS particles.

The elemental composition of NiS particles was determined by EDX spectroscopy performing spot measurements on particles. The major peaks are due to the presence of Ni along with sulphur. The elemental ratio of Ni to S in the NiS is 56:44.

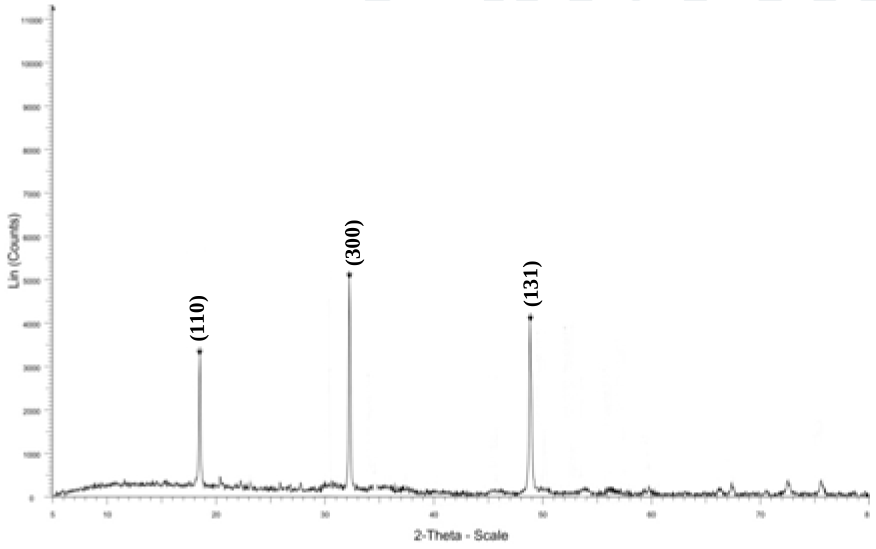


Fig 7 POWDER XRD OF THE COMPLEX $[Ni(dpdtc)_2$

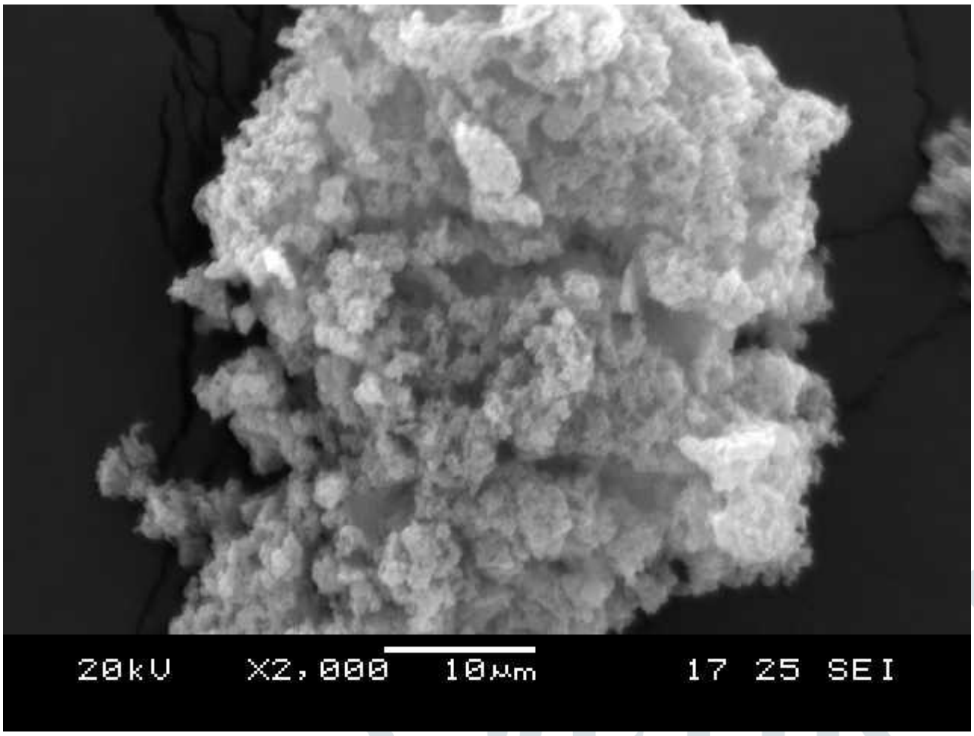


Fig 8. SEM images of nano NiS

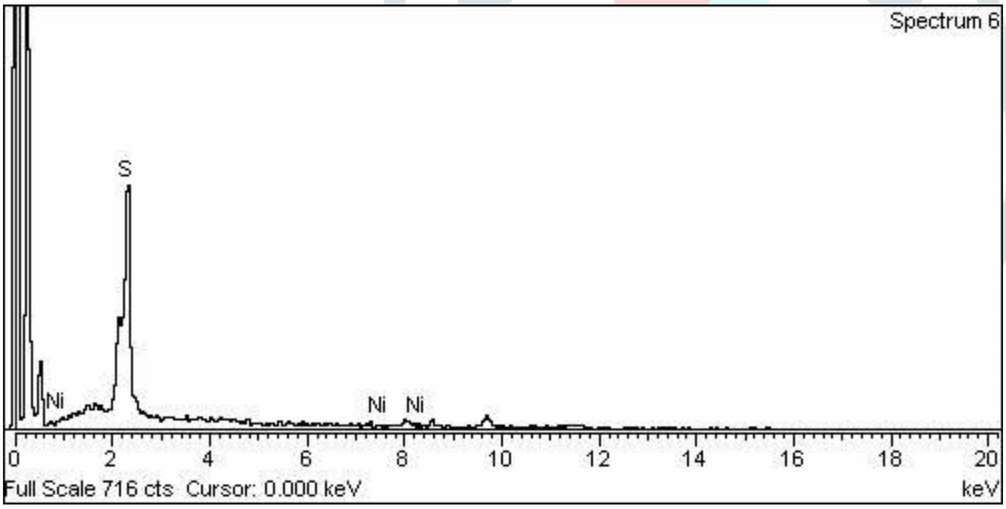
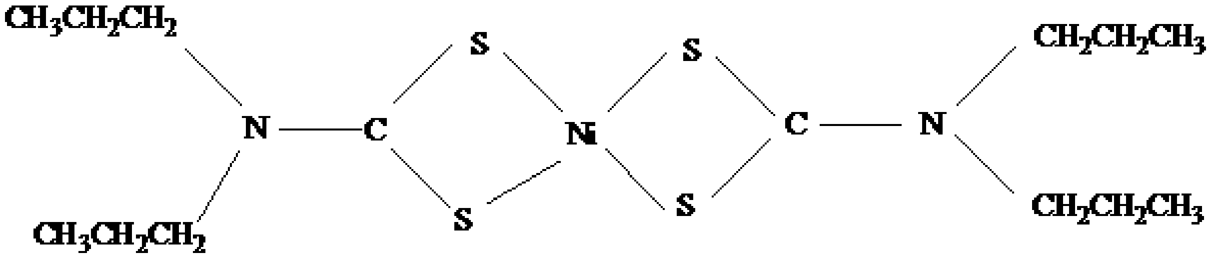


FIG. 9. THE EDX SPECTRA OF NANO NIS PARTICLES

PROPOSED STRUCTURE OF THE COMPLEX [Ni(DPDTC)$_2$]



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