

Synthesis, Characterization and Antifungal Studies of Adducts of *p*-Ethylphenyldithiocarbonates of Copper(II)

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A series of adducts of *p*-ethylphenyldithiocarbonates of copper(II) [(*p*-C₂H₅C₆H₄OCS₂)₂Cu] with ethyl pyridines and chloro pyridines have been synthesized in 1:2 molar ratio. They were characterized by elemental analysis, magnetic susceptibility and molar conductance measurements, infrared, electronic, electron spin resonance and mass spectroscopy, NMR and thermogravimetric analysis. In addition, antifungal studies of these adducts were also performed. The results revealed that the adducts have 1:2 stoichiometry, non-electrolytic and paramagnetic at room temperature. On the basis of spectral studies, a distorted octahedral geometry is proposed around copper(II) ion. ESR studies depicted elongated axial symmetry of Cu(II)adducts with nitrogen donors. Moreover, the adducts also showed potential antifungal activity against *Fusarium oxysporum*.

Keywords: Dithiocarbonates, Pyridines, Octahedral, Antifungal.

INTRODUCTION

Dithiocarbonates, commonly known as xanthates (xanthous^G = yellowish golden) are salts & ester of xanthic acid ROC(=S)SH (R = alkyl or aryl), obtained by reaction of an alcohol with sodium or potassium hydroxide and carbon disulphide. Xanthates of a large number of coordination complexes of transition and main group metals are known [1]. It has been reported that metal aryl xanthates has been successfully formed by reacting carbon disulphide with phenol in presence of metal [2,3]. Alkyldithiocarbonates were first prepared by Semeniuc *et al.* [4] and Andotra *et al.* [5]. It has been reported from a long time that dithiocarbonates are being used in the vulcanization of rubber [6], manufacturing of synthetic textiles and as fungicides [7], metalloenzymes, material precursors, flotation reagents in metallurgy and as catalysts [8-10]. Xanthates show a number of coordination modes. They can coordinate to metal in a monodentate, isobidentate or anisobidentate fashion [11-14]. Xanthates of metals have also been successfully used in preventing corrosion, as pharmaceuticals, pesticides and fungicides in agricultural processes and in treating HIV infections [15-

19]. Certain metal xanthates were also known to be potent antiviral and antitumor agents [20,21].

Copper is an essential trace element present in the body of living organisms. Copper is essential metal for living organisms because of its use in various enzyme systems, proteins and due to its enhanced synergistic effect with drugs [22]. Copper(II) forms complexes with drugs as ligands, which exhibits increased activity when compared to free drugs [23] and some complexes of copper(II) xanthate with different ligands are found to be potent antitumor [24,25] and antioxidant [26,27] agents. Presently, we are reporting the synthesis of *p*-ethylphenyldithiocarbonates of copper(II) with ethyl pyridines and chloro pyridines and their characterization by different physico-chemical and spectroscopic techniques.

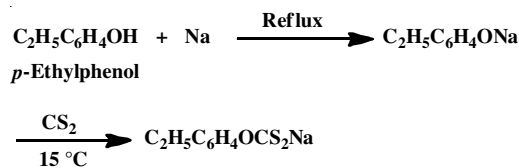
EXPERIMENTAL

Sodium salts of *p*-ethylphenyldithiocarbonates were prepared using standard protocol [28]. Toluene and *n*-hexane were freshly dried over sodium wire. Dichloromethane and methanol were dried over P₂O₅ and CaCO₃, respectively. *p*-Ethylphenol

was purified by distillation prior to use. The percentage of carbon, hydrogen, nitrogen and sulphur was estimated on elemental analyzer. A digital conductivity meter "Century CC 601" was used to measure the molar conductance of the adducts at room temperature, in dimethylformaamide (10^{-3} M). Magnetic susceptibility of the adducts synthesized, were measured at room temperature by VSM method. Infrared spectra of 1:2 addition complexes was recorded on Perkin Elmer FTIR spectrophotometer in the region $4000-400\text{ cm}^{-1}$. The electronic (UV) spectra was recorded on Systronics 119 UV-visible Spectrophotometer in the range of $12500-40000\text{ cm}^{-1}$. ESR of adducts was recorded on JES-FA200 ESR spectrometer with X band. Mass spectra of the compounds was recorded on electron spray ionization mass (ESI-MS) spectrophotometer. Thermogravimetric analysis (TGA/DTA) was carried out on Linseis STA-PT-thermo analyzer. The complex was heated at the rate of $10\text{ }^{\circ}\text{C}/\text{min}$ in the temperature range of $25-1000\text{ }^{\circ}\text{C}$.

Preparation of sodium salt of *p*-ethylphenyldithiocarbamate:

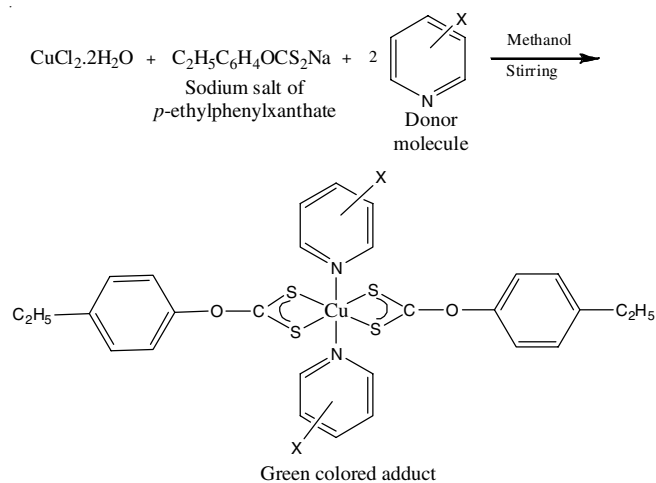
To a toluene solution of freshly distilled *p*-ethylphenol (31.7 mL, 0.26 mol) was added sodium metal (0.74 g, 0.26 mol). The contents were refluxed for 3 h till white precipitates were formed and sodium metal was completely dissolved. Subsequently, to the reaction mixture was added CS_2 (1.95 mL, 0.26 mol) at $15\text{ }^{\circ}\text{C}$ and the contents were stirred for 2-3 h during which the colour of the mixture changed to yellow. The compound was filtered using alkoxy funnel fitted with G-4 sintered disc. The yellow coloured salt formed was washed with *n*-hexane and then dried in a vacuum dessicator that gives the compound $p\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{OCS}_2\text{Na}$ as pale yellow solid. The reaction is as under:



Preparation of adducts of *bis*(*p*-ethylphenyldithiocarbato)copper(II) with ethylpyridines and chloropyridines:

The addition complexes of copper(II) were obtained by the direct reaction of methanolic solution of metal salt, sodium salt of *p*-ethylphenyldithiocarbamate and substituted pyridines. A 20 mL solution of cupric chloride dihydrate (0.42 g, 0.0026 mol) in methanol was prepared. To this solution, a sodium salt of *p*-ethylphenyldithiocarbamate (1.14 g, 0.0052 mol) and a pyridine molecule (0.0052 mol) [2-ethylpyridine = 0.59 g, 3-ethylpyridine = 0.59 g, 4-ethylpyridine = 0.59 g, 2-chloropyridine = 0.49 g, 3-chloropyridine = 0.49 g] dissolved in 40 mL methanol was slowly added and stirred constantly for 1 h. The precipitates so obtained, were collected on G-4 sintered funnel. The precipitates were washed with methanol followed by drying in vacuum, which yielded the green coloured complex.

Antifungal studies: The antifungal studies of some adducts synthesized were performed by poisoned food technique against the fungal strain *Fusarium oxysporium* using Potato Dextrose Agar (PDA) as the nutrient medium. The adducts dissolved in DMF were added to nutrient medium. It was then discharged into sterile petri dishes inside the laminar flow and left to solidify. After solidification, the spores of the fungus were suspended



Scheme-I: Method of preparation and proposed structure of 1:2 addition complex of *bis*(*p*-ethylphenyldithiocarbato)copper(II); X = ethyl (C_2H_5) or chloro (Cl)

using a cork borer (6 mm in diameter) at the center of petri-dishes on the PDA medium. The petri dishes were incubated for 96 h at $27\text{ }^{\circ}\text{C}$ which were used as control. The radial growth of fungus determines the efficiency of each test sample. The linear fungal growth in controlled manner was measured at various concentrations of the adducts. The formula to calculate the per cent inhibition of the fungus over control is:

$$I = \frac{C - T}{C} \times 100$$

where I is % inhibition, C is the fungal colony diameter in the control plate after the incubation time of 96 h and T is the fungal colony diameter in the tested plate after 96 h.

RESULTS AND DISCUSSION

The addition complexes of *bis*(*p*-ethylphenyldithiocarbato)copper(II) are dark green microcrystalline solids. These are soluble in dimethyl formamide and dimethyl sulfoxide, but are insoluble in acetone, benzene, carbon tetrachloride and ethanol. Elemental analysis showed that the adducts formed have 1:2 stoichiometry having the general formula $[\text{Cu}(p\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{OCS}_2)_2\text{L}_2]$ [where, L = 2-, 3-, 4-ethyl pyridine and 2-, 3-chloro pyridine] (Table-1).

Molar and magnetic measurements: The values of molar conductance of the adducts dissolved in DMF lies in the range $12.81-19.20\text{ ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$ and the range of magnetic moment values of 1:2 complexes of *bis*(*p*-ethylphenyldithiocarbato)copper(II) with ethyl and chloro pyridines is 1.79-1.92 B.M (Table-1). The molar conductance values of adducts prepared in dimethylformaamide are much lower than that for a univalent electrolyte in this solvent indicating the non-electrolytic nature of adducts [29,30]. The values of magnetic moment for adducts agrees well with values of magnetic moment reported for the distorted octahedral complexes of copper(II) [31]. These values confirms the paramagnetic nature of adducts.

Infrared spectra: A free dithiocarbamate shows vibrations due to $\nu(\text{C-O-C})$ stretching in the range of $1280-1270\text{ cm}^{-1}$ and the $\nu(\text{C-S})$ stretching vibration exhibits two bands in the range of $1070-1057\text{ cm}^{-1}$. In the present work, $\nu(\text{C-S})$ gives a single sharp band (without a shoulder) of high intensity for

TABLE-1
MOLAR CONDUCTANCE, MAGNETIC MOMENTS AND ANALYTICAL DATA OF 1:2 ADDITION COMPLEXES OF
BIS(*p*-ETHYLPHENYLDITHIOCARBONATO)COPPER(II) WITH SUBSTITUTED PYRIDINES

| Name of the adduct | Elemental analysis (%): Found (calcd.) | | | | Molar conductance (ohm ⁻¹ mol ⁻¹ cm ²) | μ_{eff} (B.M.) 298 K |
|--|---|-----------|-----------|-------------|---|---------------------------------------|
| | C | H | N | S | | |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (2-ethylpyridine)copper(II) | 51.2 (57.0) | 4.1 (5.3) | 3.8 (4.1) | 17.9 (19.0) | 16.20 | 1.80 |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (3-ethylpyridine)copper(II) | 50.4 (57.0) | 4.0 (5.3) | 3.6 (4.1) | 18.2 (19.0) | 12.81 | 1.79 |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (4-ethylpyridine)copper(II) | 51.7 (57.0) | 4.5 (5.3) | 3.6 (4.1) | 18.4 (19.0) | 13.66 | 1.83 |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (2-chloropyridine)copper(II) | 39.0 (42.8) | 3.0 (3.3) | 3.3 (3.5) | 15.0 (16.3) | 18.40 | 1.85 |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (3-chloropyridine)copper(II) | 38.3 (42.8) | 3.1 (3.3) | 3.1 (3.5) | 15.3 (16.3) | 19.20 | 1.92 |

the adducts in the range of 1067-1042 cm⁻¹ (Table-2), which suggests symmetrical bidentate binding of dithiocarbonate moiety with copper atom. Moreover, the band for $\nu(\text{C-S})$ vibrations in the complexes prepared shifts towards the lower frequency region (higher wavelength) in comparison to free dithiocarbonate ligands, which may also be attributed to symmetrical bidentate binding of dithiocarbonates. On complex formation, the out of plane C-H bands shifts towards lower frequency region showing red shift, which confirms that metal ion is attached to the pyridine molecule through its ring nitrogen atom. A band in the region 1260-1224 cm⁻¹ is due to $\nu(\text{C-O-C})$ of dithiocarbonate moiety. A medium to strong intensity band in the range 378-343 cm⁻¹ was observed which may be attributed to Cu-S stretching mode [32].

Electronic spectra: The electronic spectra of adducts of *bis*(*p*-ethylphenyldithiocarbonato)copper(II) have been obtained in DMF. These adducts of copper(II) showed a broad absorption band appearing at 12585-15395 cm⁻¹, which is assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition as expected for six coordinate d^9 species (Table-2, Figs. 1 and 2). So, a distorted octahedral geometry is suggested for these copper(II) complexes [33,34].

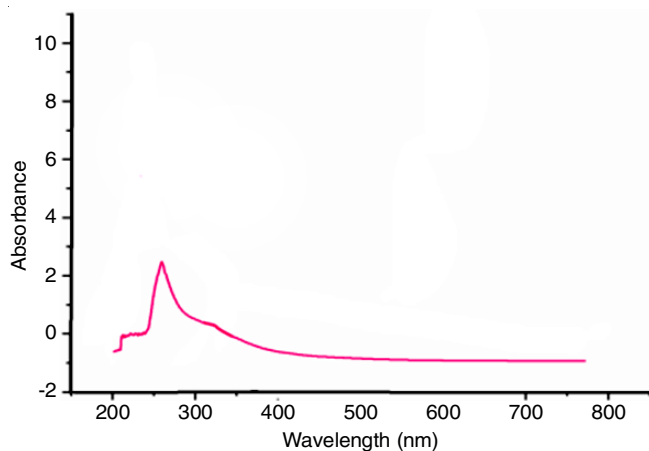


Fig. 1. Electronic spectra of *bis*(*p*-ethylphenyldithiocarbonato)*bis*(2-ethylpyridine)copper(II)

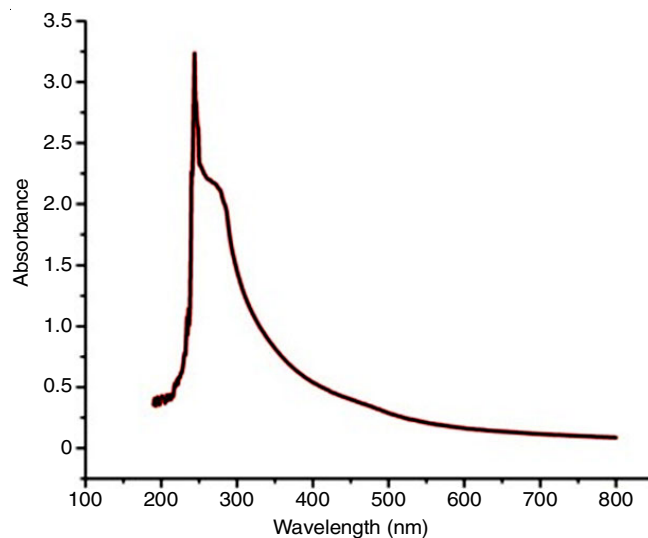


Fig. 2. Electronic spectra of *bis*(*p*-ethylphenyldithiocarbonato)*bis*(2-chloropyridine)copper(II)

Electron spin resonance spectra: X-band ESR spectra of all the complexes were recorded in DMF at room temperature. All Cu(II) adducts with nitrogen donors exhibits g_{\parallel} and g_{\perp} components with axial symmetry. The complex $[\text{Cu}(p\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{OCS}_2)_2(\text{C}_7\text{H}_9\text{N})_2]$ exhibits $g_{\parallel} = 2.250$, $g_{\perp} = 2.034$ and $g_{\parallel} = 2.181$, $g_{\perp} = 2.042$ for the complex $[\text{Cu}(p\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{OCS}_2)_2(\text{C}_5\text{H}_4\text{NCl})_2]$ (Fig. 3).

In ESR spectra of the synthesized adducts, $g_{\parallel} > g_{\perp}$ which indicates a slight elongation along z -axis thus, representing elongated axial symmetry of the coordination sphere around Cu(II) ion. Here, $g_{\parallel} > g_{\perp} > 2.0023$ shows substantial parallel hyperfine splitting and the ground state is $d_{x^2-y^2}$ [35].

Mass spectra: The mass spectra of the adducts of *bis*(*p*-ethylphenyldithiocarbonato)copper(II) with ethylpyridines and chloropyridines was recorded. The mass spectra of the complex $\text{Cu}(\text{S}_2\text{COC}_6\text{H}_4\text{C}_2\text{H}_5)_2(3\text{-chloropyridine})_2$ showed a weak molecular ion peak at m/z 684.5 (Fig. 4). The occurrence of molecular ion peak $[\text{M}]^+$ at this value indicates that the comp-

TABLE-2
UV AND IR SPECTRAL DATA OF 1:2 ADDITION COMPLEXES OF
BIS(*p*-ETHYLPHENYLDITHIOCARBONATO)COPPER(II) WITH SUBSTITUTED PYRIDINES

| Name of the adduct | ν (cm ⁻¹) ($e_g \rightarrow t_{2g}$) | $\nu(\text{C-S})$ | $\nu(\text{C-O-C})$ | Aromatic stretching | | $\nu(\text{Cu-S})$ |
|--|---|-------------------|---------------------|---------------------|-------------------|--------------------|
| | | | | $\nu(\text{C-H})$ | $\nu(\text{C-C})$ | |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (2-ethylpyridine)copper(II) | 13587 | 1055 | 1242 | 3030 | 1594 | 354 |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (3-ethylpyridine)copper(II) | 12890 | 1042 | 1250 | 3024 | 1596 | 357 |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (4-ethylpyridine)copper(II) | 12585 | 1067 | 1230 | 3046 | 1601 | 343 |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (2-chloropyridine)copper(II) | 14489 | 1060 | 1224 | 3026 | 1597 | 378 |
| <i>Bis</i> (<i>p</i> -ethylphenyldithiocarbonato) <i>bis</i> (3-chloropyridine)copper(II) | 15395 | 1051 | 1247 | 3041 | 1599 | 361 |

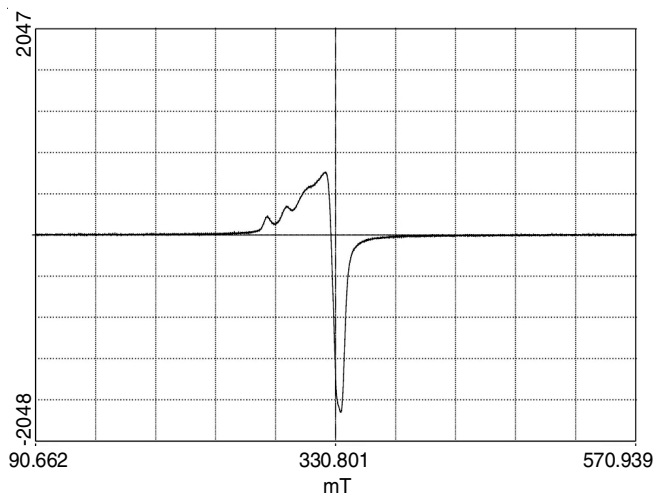


Fig. 3. ESR spectra of *bis(p-ethylphenyldithiocarbonato)bis(2-ethylpyridine)copper(II)*

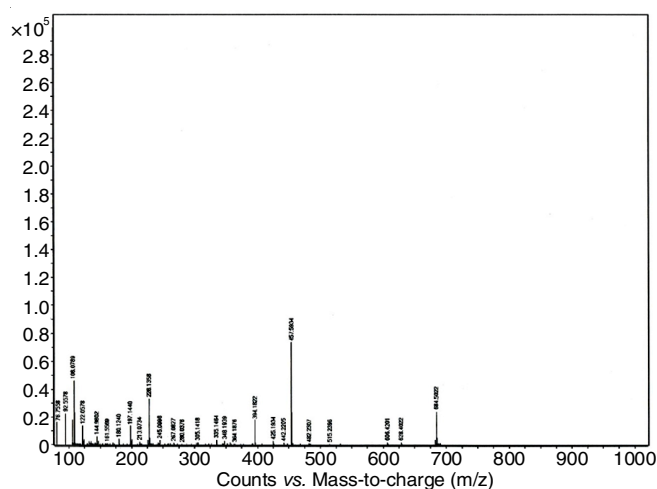


Fig. 4. Mass spectra of *bis(p-ethylphenyldithiocarbonato)bis(3-chloropyridine)copper(II)* ($m/z = 684.5$)

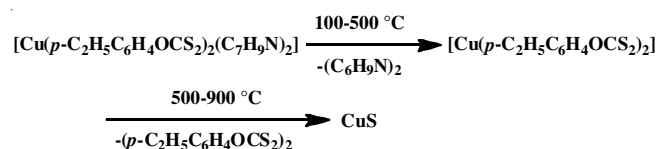
lexes formed are monomeric. The base peak for this complex appeared at m/z 457.5 which corresponds to the fragment $[\text{Cu}(\text{S}_2\text{COC}_6\text{H}_4\text{C}_2\text{H}_5)_2]^+$. It suggests the formation of copper(I) xanthate as the most stable fragment in the mass spectral studies of the adducts of Cu(II).

^1H NMR: The ^1H NMR spectra of these addition complexes in deuterated DMSO gave characteristic proton resonances.

In this spectra, the signals for $-\text{CH}_2\text{CH}_3$ (ethyl group) on the benzene ring were observed at 1.26 ppm as triplet (for $-\text{CH}_3$) and at 2.63 ppm as quartet (for $-\text{CH}_2$). The protons of C_6H_4 in the copper(II) complexes gave signals with splitting in the range 6.82-7.10 ppm. The ring protons of *para* complexes give two resonances. In case of ethylpyridines and chloropyridines, the protons of pyridine ring gave signals in the range 7.16-8.49 ppm and ethyl group absorbs at 0.98 ppm as triplet ($-\text{CH}_3$) and at 2.76 ppm as quartet ($-\text{CH}_2$) (Table-3).

^{13}C NMR: ^{13}C NMR of the addition complexes exhibited chemical shifts for all carbons in their characteristic regions. The signal for ethyl group occurred at 14.27 ppm (for $-\text{CH}_3$) and at 28.35 ppm (for $-\text{CH}_2$). The carbon nuclei of phenyl group (C_6H_4) gave the resonance in the region 114.03-130.89 ppm. The carbon attached to the ethyl group appeared at 122.70-134.50 ppm. The ethylphenyl derivatives gave signal in the region 151.30-152.99 ppm. The chemical shift for the carbon nuclei of dithiocarbonate moiety ($-\text{OCS}_2$) was observed at 166.95-185.68 ppm, shifting it upfield (30-36 ppm) in comparison with the parent ligand. The aryl carbon nuclei of the pyridines show three resonances in the region 123.34-151.83 ppm (Table-4).

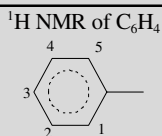
Thermogravimetric analysis: The TG of the complex [*bis(p-ethylphenyldithiocarbonato)bis(2-ethylpyridine)-copper(II)*] i.e., $[\text{Cu}(p\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{OCS}_2)_2(\text{C}_7\text{H}_9\text{N})_2]$ showed an initial weight loss of 34.82 % (calculated = 32.08 %) at 394.5 °C by loosing two molecules of 2-ethylpyridine. On further heating, a weight loss of 62 % (calculated = 62.2 %) at 661.8 °C due to the loss of two xanthate moieties was observed. The gradual loss in weight gave a stable sulphide, CuS at 900 °C (Fig. 5).



The TG of [*bis(p-ethylphenyldithiocarbonato)bis(2-chloropyridine)copper(II)*] i.e., $[\text{Cu}(p\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{OCS}_2)_2(\text{C}_5\text{H}_4\text{NCl})_2]$ showed an initial weight loss of 32.2 % on heating (calculated = 33 %) at 531.4 °C due to the loss of two molecules of 2-chloropyridine. Further heating of complex results in the weight loss of 57.2 % (calculated = 57.5 %) at 874.4 °C by loosing

TABLE-3
 ^1H NMR SPECTRAL DATA OF 1:2 ADDUCTS OF
BIS(p-ETHYLPHENYLDITHIOCARBONATO)COPPER(II) WITH SUBSTITUTED PYRIDINES

| $-\text{CH}_2-\text{CH}_3$ | ^1H NMR of C_6H_4 | Donor moiety |
|---|--|---|
| 1.26, t, 6H (CH_3); 2.63, m, 4H (CH_2) | 6.92, d, 4H, [$\text{H}_{(1,5)}$]; 6.83, d, 4H, [$\text{H}_{(2,4)}$] | 7.19-8.40, m, 8H, (NC_5H_4); 0.97, t, 6H, (CH_3); 2.76, m, 4H, (CH_2) |
| 1.28, t, 6H, (CH_3); 2.62, m, 4H (CH_2) | 7.10, d, 4H, [$\text{H}_{(1,5)}$]; 6.80, d, 4H, [$\text{H}_{(2,4)}$] | 7.22-8.39, m, 8H (NC_5H_4); 1.20, t, 6H (CH_3); 2.67, m, 4H, (CH_2) |
| 1.26, t, 6H (CH_3); 2.61, m, 4H (CH_2) | 6.98, d, 4H, [$\text{H}_{(1,5)}$]; 6.72, d, 4H, [$\text{H}_{(2,4)}$] | 7.31-8.41, m, 8H, (NC_5H_4); 0.99, t, 6H (CH_3); 2.74, m, 4H (CH_2) |
| 1.25, t, 6H (CH_3); 2.63, m, 4H (CH_2) | 7.08, d, 4H, [$\text{H}_{(1,5)}$]; 6.87, d, 4H, [$\text{H}_{(2,4)}$] | 7.45-8.41, m, 8H (NC_5H_4) |
| 1.27, t, 6H (CH_3); 2.63, m, 4H (CH_2) | 6.90, d, 4H, [$\text{H}_{(1,5)}$]; 6.72, d, 4H, [$\text{H}_{(2,4)}$] | 7.32-8.49, m, 8H (NC_5H_4) |



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