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Synthesis and Characterization of Adducts of Bis(*o*-isopropyldithiocarbonato) Copper (II) with Substituted Pyridines and their Biological Studies

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ABSTRACT

A series of adducts of Bis (O-isopropyldithiocarbonato) copper (II) with substituted pyridines have been synthesized by treating Bis(O-isopropyldithiocarbonato)copper(II) with substituted pyridines in acetone in equimolar ratios. Analytical results show that the adducts have 1:1 stoichiometry with general formula Cu(O-isopropyldithiocarbonato)$_2$L where L=2 and 3-bromopyridine; 4-acetylpyridine; 3-hydroxypyridine; 2–methoxypyridine; 2-amino-3-methylpyridine; 2-amino-4-methylpyridine; 2-amino-5-methylpyridine). The addition complexes have been characterized by elemental analysis, conductivity measurements and magnetic susceptibility measurements, infrared and electronic spectral studies. These studies suggest a trigonal bipyramidal structure and paramagnetic nature of the adducts. Antifungal activity of some adducts have been carried out against the fungal strain Fusarium oxysporium.

Keywords: O-isopropyldithiocarbonate; Fusarium oxysporium

INTRODUCTION

Metallic derivatives of RO–CS^{2-} ligands have been known since 1815, but their synthetic and structural chemistry witnessed increased attention through pioneering work of Hoskins and Winter and others [1]. These have been extensively used as pharmaceuticals, fungicides, pesticides, rubber accelerators, corrosion inhibitors, agricultural reagents and quite recently in therapy for HIV infections [2]. Metal xanthates are weel known agents in the flotation of minerals of transition metals such as copper, zinc, cobalt and nickel and in the separation and quantitive determination of large number of cations [3,4]. The use of cellulose xanthate for the column for the separation of alcohols by chromatographic method is one of excellent application of metal xanthate [5]. Sodium and potassium ethyl xanthate have antidotal effects in acute mercury poisoning. Transition metal xanthate complexes have been investigated for nonlinear optical applications [6].

EXPERIMENTAL SECTION

The potassium salts of O-alkyldithiocarbonates were prepared by the standard published method [7].

Potassium Salt of O-isopropyldithiocarbonate

Potassium hydroxide pellets 4.2 g (0.075 mol) were dissolved in isopropyl alcohol 15.6 g (19.4 ml, 0.26 mol) in a round bottom flask and refluxed for one hour. The reaction mixture was allowed to cool and the solution was decanted off from the residual solid into a beaker. To the resulting solution, carbon disulfide 5.7 g (4.5 ml, 0.075 mol) was added drop wise and with constant stirring. The reaction mixture was allowed to cool in an ice bath and the resulting solid mass was filtered on a sintered glass funnel at the pump, washed it with three 2.5 ml portions of ether, dried in vacuum desiccator and recrystallized from absolute ethanol.

Preparation of Complexes

All the attempts to isolate stable complexes of bis(O-alkyldithiocarbonato)copper(II) resulted in the isolation of corresponding bis(O-alkyldithiocarbonato)copper(I). However, rather than proceeding with the parent compounds, when the reactants i.e, cupric chloride dihydrate, potassium salts of O-alkyl dithiocarbonates and nitrogen donor ligands were mixed in the ratio of 1:2:1 in acetone, the formation of stable adducts of bis(O-alkyldithiocarbonato) copper(II) were observed as confirmed by various physico-chemical techniques and spectroscopic studies.

Preparation of the Adducts

A solution of $CuCl_2.2H_2O$ (0.42 g, 0.0026 mol) was prepared in acetone. To this solution, was added a solution of potassium salt of O-isopropyldithiocarbonate (0.74 g, 0.0052 mol) and substituted pyridine (0.0026 mol) which was prepared in 50 ml acetone. The mixture was stirred for 30 minutes when green precipitates were obtained which were filtered immediately and dried in a vacuum desiccator over anhydrous calcium chloride. Various substituted pyridines used are [2- bromopyridine=0.410 g; 3-bromopyridine= 0.410 g; 4-acetylpyridine =0.314 g; 3-hydroxypyridine = 0.247 g; 2-methoxypyridine= 0.287 g; 2-amino-3-methylpyridine=0.2511g; 2-amino-4-methylpyridine=0.2511 g ; 2-amino-5-methylpyridine= 0.2511 g (0.0026 mol)] for 30 min. The contents of the reaction mixture were allowed to stand for20-24 h and the green obtained was washed with the solvent used in their preparation and dried over calcium chloride at room temperature.

Methods

Carbon, Hydrogen, Nitrogen and Sulfur were determined on elemental analyzer (elemental vario EL III, carlo Erba 1108). Molar conductance was determined on the millimolar solution in DMF using century CC 601 Conductivity Bridge. Infrared spectra of the complexes over the region 4,000-200 cm21 were recorded using KBr pellets on Infrared spectrophotometer (Perkin Elmer FT-IR). The electronic spectra of the adducts were recorded in DMF on systronics 119 UV–visible spectrophotometer. Magnetic moments were determined at room temperature by VSM method (Princeton Applied Research-Model No. 155). The analytical data, molar conductance and magnetic moments of the adducts isolated are presented in Tables.

RESULTS AND DISCUSSION

Preliminary Investigations

The adducts of bis(O-isopropyldithiocarbonato) copper(II) with various nitrogen donor ligands are bright green microcrystalline solids. Elemental analysis reveals that the adducts isolated have 1:1 stoichiometry with general formula, $(Cu(S_2COC_3H_7)_2(L))$, (L=2-, 3-bromopyridine, 4-acetylpyridine, 3-hydroxypyridine, 2-methoxypyridine, 2-aminp-3-methylpyridine, 2-amino-4-methylpyridine and 2-amino-5-methylpyridine). The adducts are insoluble in common organic solvents such as acetone, 1, 4-dioxane, nitrobenzene, ethanol, methanol etc. However in some organic solvents like dimethylsulfoxide and dimethyformamide, adducts are quite soluble. The parent complexes i.e copper (II)dithiocarbonates are highly unstable and get reduced to corresponding copper(I) dithiocarbonate, the adducts are fairly stable in air. However, various physico-chemical investigations show that as compared to parent complexes i.e, copper(II)xanthates which are unstable and readily gets reduced to the corresponding copper(I)xanthates, the adducts synthesized are fairly stable in air. The analytical data of the adducts of bis(O-alkyldithiocarbonato)copper(II) with various nitrogen donor ligands are summarized in Table 1.

Table 1: Analytical data of the adducts of bis(o-isopropyldithiocarbonato)copper (ii)with nitrogen donor ligands

S. No	Name of the adduct	Mol. Wt.	% Yield	Colour	%age (Found)				%age (Calculated)			
					C	H	N	S	C	H	N	S
1	Bis(O-isopropyldithiocarbonato) (2-bromopyridine)copper(II)	491.4	75	Green	31.15	3.25	2.18	25.89	31.74	3.66	2.85	26.05
2	Bis(O-isopropyldithiocarbonato) (3-bromopyridine)copper(II)	491.4	80	Green	31.2	3.11	2.2	25.91	31.74	3.66	2.85	26.05

3	Bis(O-isopropyldithiocarbonato) (4-acetylpyridine)copper(II)	454.5	81	Green	39.12	4.01	2.99	27.95	39.6	4.62	3.08	28.16
4	Bis(O-isopropyldithiocarbonato) (3-hydroxypyridine)copper(II)	428.5	77	Green	35.81	4.1	2.99	29.16	36.4	4.43	3.27	29.87
5	Bis(O-isopropyldithiocarbonato) (2-methoxypyridine)copper(II)	442.5	88	Green	37.13	4.35	2.94	28.99	37.97	4.75	3.16	28.93
6	Bis(O-isopropyldithiocarbonato) (2-amino-3-methylpyridine)copper(II)	441.5	75	Green	37.96	4.21	6.12	28.42	38.05	4.98	6.34	28.99
7	Bis(O-isopropyldithiocarbonato)(2-amino-4-methylpyridine)copper(II)	441.5	74	Green	37.85	4.41	5.99	28.21	38.05	4.98	6.34	28.99
8	Bis(O-isopropyldithiocarbonato)(2-amino-5-methylpyridine)copper(II)	441.5	79	Green	37.92	4.01	6.12	28.54	38.05	4.98	6.34	28.99

Physico-Chemical and Spectroscopic Investigations

Molar conductance measurements:

The molar conductance measurements of the millimolar solutions of the adducts of bis(O-isoproyldithiocarbonato)copper (II), carried out in dimethylformamide suggest that the adducts synthesized are non-electrolytic in nature. The molar conductance values of all the adducts have been found to lie in the range of 10.84-24.63 ohm^{-1}mol^{-1}cm^{2}. These values are lower than the values expected for any uni-univalent electrolytes in this solvent suggesting that these complexes are neutral and non-ionic in character[8]**.** The molar conductance values of the adducts are given in Table 2.

Magnetic measurements:

The adducts of bis(O-isopropyldithiocarbonato)copper(II) with various nitrogen donor ligands exhibit magnetic moment in the range of 1.81-1.92 B.M (Table 2). These values are in agreement with magnetic moment values observed in many square pyramidal complexes of copper (II) [9-11]. The observed magnetic moment values are greater than the spin only magnetic moment values showing that there is appreciable orbital contribution and the unpaired electron is in the d$_{x2-y2}$ orbital. These values also suggest that there are no direct metal-metal interactions which is reflected by absence of hyperfine splitting in the ESR spectra of the adducts synthesized.

Table 2: Molar conductance and mgnetic data of the adducts of Bis(o-isopropyldithiocarbonato)copper(ii) with nitrogen donor ligands

S. No.	Name of the Adduct	Molar Conductance (Ohm^{-1} mol^{-1} cm^{2})	Magnetic Data	
			μ$_{eff}$(B.M)	Temperature
1	Bis(O-isopropyldithiocarbonato)(2-bromopyridine)copper(II)	16.81	1.82	298
2	Bis(O-isopropyldithiocarbonato)(3-bromopyridine)copper(II)	14.63	1.81	298
3	Bis(O-isopropyldithiocarbonato)(4-acetylpyridine)copper(II)	15.6	1.9	298
4	Bis(O-isopropyldithiocarbonato)(3-hydroxypyridine)copper(II)	24.63	1.92	298
5	Bis(O-isopropyldithiocarbonato)(2-methoxypyridine)copper(II)	13.5	1.89	298
6	Bis(O-isopropyldithiocarbonato)(2-amino-3-methylpyridine)copper(II)	21.51	1.86	298
7	Bis(O-isopropyldithiocarbonato)(2-amino-4-methylpyridine)copper(II)	20.3	1.91	298
8	Bis(O-isopropyldithiocarbonato)(2-amino-5-methylpyridine)copper(II)	21.13	1.83	298

Spectral Studies

Infrared spectra:

The IR spectra of the adducts of bis(O-alkyldithiocarbonato)copper(II) with nitrogen donor ligands such as 2-bromopyridine, 3-bromopyridine, 4-acetylpyridine, 3-hydroxypyridine, 2-methoxypyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine and 2-amino-5-methylpyridine were recorded in the range of 4000-200cm^{-1}. The important infrared peaks which are useful in establishing the geometry of the adducts are tabulated in Tables 3. IR spectra of the adducts of copper(II) dithiocarbonates with various nitrogen donors show sharp bands in the region 1198-1220 cm^{-1} and 1137-1150 cm^{-1} corresponding to asymmetric and symmetric stretching of C-O-C group[12,13]**.** The appearance of single band corresponding to ν(C-S) stretching vibration suggests that xanthate is binding the metal ion as symmetrical bidentate chelating ligand. A new band of medium to strong intensity, observed in the range of 320-352 cm^{-1}, may be attributed to Cu-S stretching mode[14]**.** A comparison of the infrared spectral data of the adducts of Cu[(S$_2$COR)$_2$.L] [L= 2-,3-bromopyridine, 4-acetylpyridine, 3-hydroxypyridine, 2-methoxypyridine, 2-aminp-3-methylpyridine, 2-amino-4-methylpyridine and 2-amino-5-methylpyridine] with those of the free ligands reveals that characteristic bands corresponding to C-H out of plane bending vibrations of the free ligand show a slight negative shift (5-10 cm^{-1}) in their respective adducts[15]**.** However, a considerable positive shift in the characteristic vibrations such as ring C-C, C-N stretching vibrations, C-H in plane and ring in and out of plane stretching vibrations were observed. In case of adducts of bis(O-alkyldithiocarbonato)copper(II) with substituted pyridines, strong bands corresponding to C-N and C-C stretching vibrations are observed in the range 1630-1580 cm^{-1} and 1470-1484 cm^{-1}. As compared to free bases these bands show considerable positive shift due to extensive π bonding between metal ion and the ligand [16]. In the adducts of bis(O-alkyldithiocarbonato)copper(II) with 2-bromopyridine, the frequency at 614 cm^{-1} has been attributed to C-Br stretching. Beside the normal ring stretching vibrations a strong band due to C-Br stretching vibration is also observed in the range of 600-650 cm^{-1} in all the adducts synthesized [17-19]. Similarly in adducts of bis(O-alkyldithiocarbonato)copper(II) with 2-methoxypyridine, the band at 3094 cm^{-1} is assigned to C-H stretching vibrations of aromatic ring. The strong band at 1022 cm^{-1} in free ligand is assigned to O-CH_3 stretching mode which is displaced to lower frequency on coordination to metal ion [20,21]. The peak at 1608 cm^{-1} in adduct with 3-hydroxypyridine is attributed to the stretching vibration of the C=N group in the pyridine ring which shifts to higher frequencies that may suggest the formation of coordination bond between the metal ion and nitrogen atom of heterocyclic ring. Complexes with 3-hydroxypyridine show strong band corresponding to ν(O-H) vibration [22,23]. In 4-acetylpyridine adducts, since the compound possess a CH_3 group. The C-H stretching vibration of methyl group occurs at lower frequencies than those of the aromatic ring [24]. In all the adducts it has been observed that the characteristic bands due to C-H bending vibrations however show considerable negative shift, thereby conforming the coordination of ligands through their ring nitrogen to the metal ion. The coordination of Lewis bases with metal ions effects C-N vibrations more as compared to C-C vibrations. These observations clearly establish the coordination of nitrogen donors with metal ion through ring nitrogen.

Table 3: Important infrared bands (cm-1) of the adducts of bis(o-isopropyldithiocarbonato)copper(ii) with nitrogen donor ligands

S.No	Name of the Adducts	Formula	ν(C-S)	ν_{as} (C-O-C)	ν_{s} (C-O-C)	ν (Cu-S)
1	Bis(O-isopropyldithiocarbonato)(2-bromopyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_5H_4N.Br)$	1031	1210	1138	338
2	Bis(O-isopropyldithiocarbonato)(3-bromopyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_5H_4N.Br)$	1030	1215	1142	329
3	Bis(O-isopropyldithiocarbonato)(4-acetylpyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_7H_7NO)$	1033	1200	1146	330
4	Bis(O-isopropyldithiocarbonato)(3-hyroxypyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_5H_5NO)$	1020	1211	1131	327
5	Bis(O-isopropyldithiocarbonato)(2-methoxypyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_6H_7NO)$	1024	1214	1120	322
6	Bis(O-isopropyldithiocarbonato)(2-amino-3-methylpyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_6H_8N_2)$	1029	1220	1136	328
7	Bis(O-isopropyldithiocarbonato)(2-amino-4-methylpyridine) copper(II)	$Cu(S_2COC_3H_7)_2(C_6H_8N_2)$	1029	1209	1130	337
8	Bis(O-isopropyldithiocarbonato)(2-amino-5-methylpyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_6H_8N_2)$	1025	1215	1122	335

Electronic spectra:

The electronic spectra of the adducts of copper(II) dithiocarbonates with the various nitrogen donor ligands used were recorded in DMF in the range 12500 cm^{-1} to 40000 cm^{-1}. Copper (II) being a d^9 ion gives rise to only one free ion term ^2D which has tenfold spin and orbital degeneracy. In this paper, the intense band corresponding to d-d transition as observed in most of the copper (II) complexes is observed in the range 15500-17600 cm^{-1}. The main absorption band around 16000 cm^{-1} can be assigned to $d_{XZ,}$ $d_{YZ} \rightarrow d_{X^2-Y^2}$. A weak shoulder is associated with it due to $dz^2 \rightarrow dx^2\text{-}y^2$ transition. Third possible transition is orbitally forbidden and merges with the broad band. The relative energy order of these transitions depends upon the extent of axial ligand-metal interaction. The appearance of a single band with the intensity pattern suggests square pyramidal geometry around copper (II) ion in these 1:1 adducts [9,25]. The adducts of bis(O-isopropyldithiocarbonato) copper (II) show a broad band in the region 15500-17000 cm^{-1} (Table 4). The main absorption band around 16000 cm^{-1} can be assigned to $d_{XZ,}$ $d_{YZ} \rightarrow d_{X^2-Y^2}$. An intense band possibly due to π-π^* or n-σ^* transitions arising from coordinated ligands (xanthates) in the region above 30000cm^{-1} is also observed in the electronic spectra of the adducts synthesized.

Table 4: Electronic spectral data of the adducts of bis(o-isopropyldithiocarbonato)copper(ii) with nitrogen donor ligands

S.No	Name of the Adduct	Formula	ν^1(cm^{-1}) dxz, dyz dx^{2}y^2	C-T Transitions (cm^{-1})
1	Bis(O-isopropyldithiocarbonato)(2-bromopyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_5H_4N.Br)$	15840	35280

2	Bis(O-isopropyldithiocarbonato)(3-bromopyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_5H_4N.Br)$	15225	34280
3	Bis(O-isopropyldithiocarbonato)(4-acetylpyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_7H_7NO)$	16643	35420
4	Bis(O-isopropyldithiocarbonato)(3-hyroxypyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_5H_5NO)$	15500	39300
5	Bis(O-isopropyldithiocarbonato)(2-methoxypyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_6H_7NO)$	16890	38500
6	Bis(O-isopropyldithiocarbonato)(2-amino-3-methylpyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_6H_8N_2)$	16340	32101
7	Bis(O-isopropyldithiocarbonato)(2-amino-4-methylpyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_6H_8N_2)$	16980	36450
8	Bis(O-isopropyldithiocarbonato)(2-amino-5-methylpyridine)copper(II)	$Cu(S_2COC_3H_7)_2(C_6H_8N_2)$	17340	34560

Electron Spin Resonance Spectral Studies

The ESR spectra of the adducts of Cu(II) exhibits a resolution of parallel $g_{\parallel}$ and $g_{\perp}$ components with an axial symmetry [$g_{\parallel}$=2.099, $g_{\perp}$ =2.024 for [$Cu(S_2COC_3H_7)_2.C_5H_4N.Br$]. In this case $g_{\parallel} > g_{\perp}$ which suggest a slight elongation along one of the axis (z-axis) causing anisotropy. From the g values it is evident that the unpaired electron is localized in the $dx^2{-}y^2$ orbital and the ground state is ^2B_1g. The $g_{\parallel} < 2.3$ confirms the covalent character of the metal-ligand bond[26]**.** The *g* values obtained in the present study when compared to the g value of a free electron, 2.0023, indicates an increase of the covalent nature of the bonding between the metal ion and the ligand molecule. This typical axial symmetry with slightly different values of $g_{\parallel}$ and $g_{\perp}$ are consistent with a penta-coordinated square pyramidal structure [9,26] Figure 1.

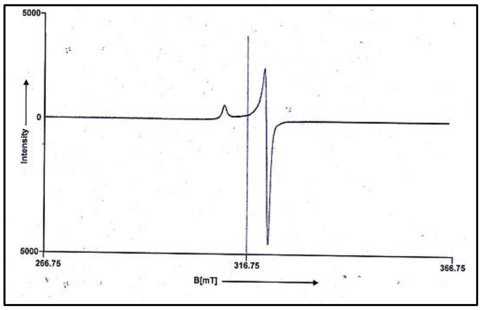

Figure 1: ESR of Bis(O-isopropyldithiocarbonato)(3-bromopyridine)copper(II)

Thermogravimetric Analysis

The adducts were subjected to TG analysis from 25°C to 1000°C in the nitrogen atmosphere. The end product in each addition complex is found to be a stable sulfide, CuS. The TGA curve of one of the adduct, $Cu(S_2COC_3H_7)_2$(3-Bromopyridine) (Figure 2) shows an initial weight loss of 30.70% (calculated=32.10%) corresponding to the removal of 3-bromopyridine molecule at 252°C. This is followed by a rapid loss of 40 % (calculated=40.37%) a xanthate moiety at 310°C. At 910°C another major loss of 86.40% (calculated=87.16%) is observed due to loss of another xanthate molecule with formation of sulphide as stable product.

$$\left[Cu(S_2COC_3H_7)_2(3\text{-bromopyridine}) \right] \xrightarrow[\substack{-3\text{-bromopyridine} \\ -\ S_2COC_3H_7}]{100\text{-}500^{o}C} \left[Cu(S_2COC_3H_7) \right. \xrightarrow{500\text{-}910^{o}C} CuS$$

Antifungal Activity

The invitro biological screening effects of the investigated compounds were tested against the pathogens *“fusarium oxysporium.”* by the poisoned food technique using potato dextrose agar (PDA) as nutrient medium [27]. The lipid membrane that surrounds the cell favours passage of only lipid soluble materials due to liphophilicity being an important factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor group. The parent compound, bis(O-alkyldithiocarbonato)copper(II) and their adducts with nitrogen donors show antifungal activity. It has been observed that the percentage inhibition caused by adduct is more than parent compound. On increasing the concentration of the complexes the colony diameter of the fungus decreases and hence percent inhibition increases. The results of biological studies are shown below (Figure 3) and data for these studies are given in Table 5.

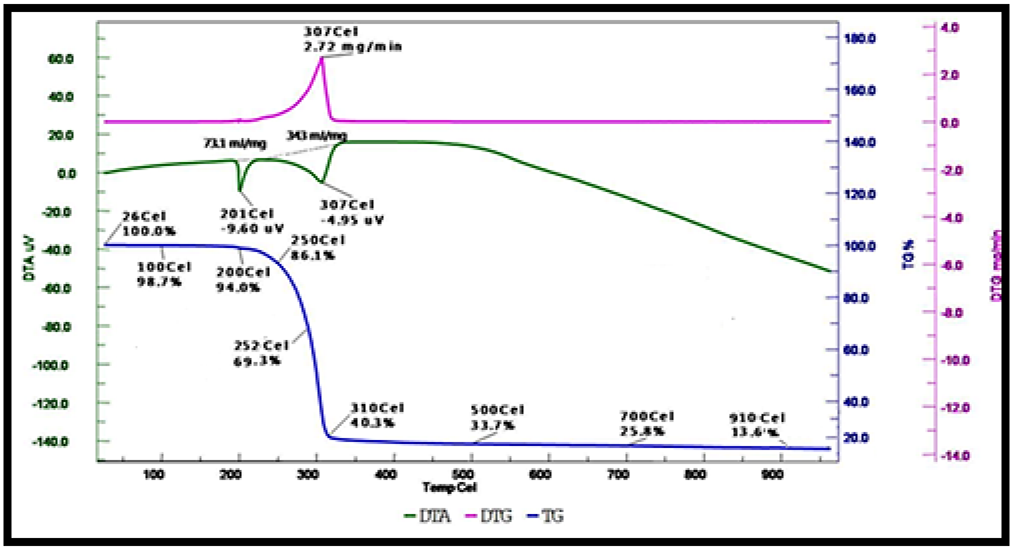

Figure 2: TGA of Cu (S2COC3H7)2(3-bromopyridine)

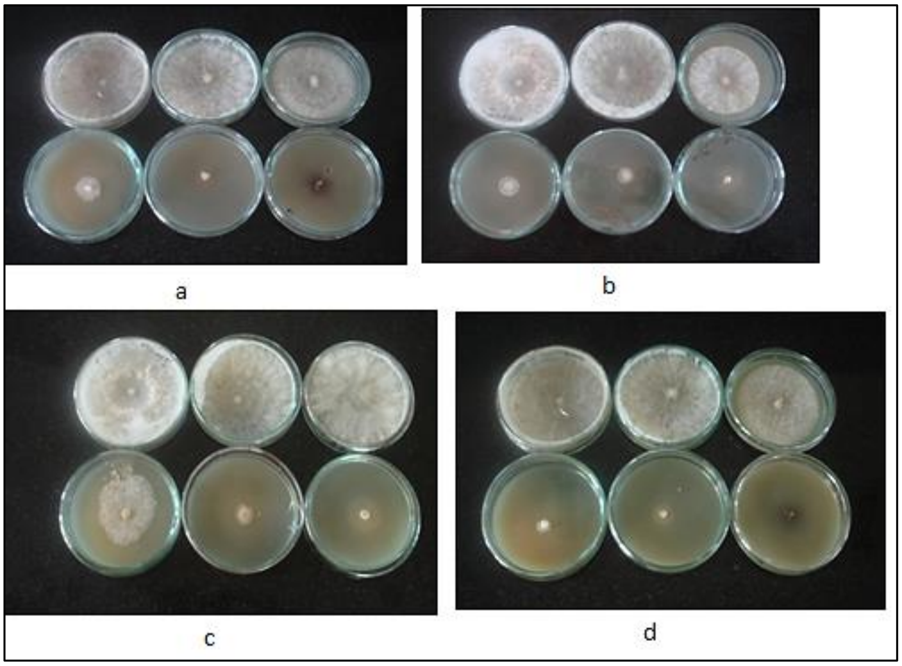

Figure 3: Antifungal activities of some adducts of copper (II)dithiocarbonate complexes against "*fusarium oxysporium*

Table 5: Antifungal activity of some bis (o-isopropylldithiocarbonato) copper (ii) against fusarium oxysporium colony diameter in control = 91 mm

S.No.	Addition Complex	Colony Diameter in Control (mm)	Concenteration (ppm)	Colony Diameter (mm)	% Inhibition I = ((C-T)/C)×100
1	(a) $Cu(S_2COC_3H_7)_2$(3-bromopyridine)		100	91	0
			200	90	1.09
			300	80	12.08
		91	400	15.01	83.5

			500	5	94.5
2	(b) $Cu(S_2COC_3H_7)_2$(4-acetylpyridine)		100	88.5	2.74
			200	64.7	28.9
			300	50.7	44.28
		91	400	15.9	82.52
			500	5	94.5
3	(c) $Cu(S_2COC_3H_7)_2$(3-hydroxypyridine)		100	91	0
			200	86	5.49
			300	81.5	10.43
		91	400	78.5	13.73
			500	5	94.5
4	(d) $(Cu(S_2COC_3H_7)_2$(2-amino-4-methyl pyridine)		100	90	1.09
			200	76	16.48
		91	300	24	73.62
			400	17	81.31
			500	5	94.5

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