OPEN ACCESS

Scholars International Journal of Chemistry and Material Sciences

Abbreviated Key Title: Sch Int J Chem Mater Sci
ISSN 2616-8669 (Print) |ISSN 2617-6556 (Online)
Scholars Middle East Publishers, Dubai, United Arab Emirates
Journal homepage: http://saudijournals.com/sijcms/

Original Research Article

Study of Antioxidant and Anticorrosion Activity of Some Microwave Synthesized *Thiourea* Derivative Ligands and Complexes

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DOI: 10.36348/sijcms.2020.v03i07.001 | **Received:** 25.08.2020 | **Accepted:** 02.09.2020 | **Published:** 15.09.2020

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Abstract

The great need to the antioxidants in our life and the increased demand of thiourea derivatives which exhibit great biological activity as anti-inflammatory, antimicrobial, antitumor, and also act as antioxidants and anticorrosive agents leads us to synthesize: N-*(2-chlorophenyl)-N'- benzoyl thiourea (CBT)* and *N-(4-chloro phenyl)-N'- benzoyl thiourea (PCBT)* by reflux method and then their metal complexes of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} were synthesized by microwave (green chemistry) in hope to get better activities. The structure of ligands and their complexes have been characterized by using elemental analysis, mass Spectroscopy, FT-IR, UV-Vis., ^{1}HNMR and ^{13}CNMR. In this study the synthesized compounds were evaluated for their *in vitro* DPPH radical scavenging activity. They exerted varying degree of scavenging activity toward DPPH radical with IC_{50} values between 84 and 250 µg/mL which is considered good and acceptable activity when compared with the activity of standard Ascorbic acid which give IC_{50} = 14.4 µg/mL. Also the anticorrosion activity of the two synthesized ligands (CBT) and (PCBT) was evaluated on carbon steel coupons by using weight loss method.

Keywords: Antioxidant activity**,** DPPH radical scavenging, thiourea derivatives, transition metal complexes, Anticorrosion activity, weight loss method.

INTRODUCTION

The reactive oxygen species, which include superoxide anions (O_2^-), hydrogen peroxide (H_2O_2) and hydroxyl radicals (OH), and Lipid peroxidation, which involves a series of free radical mediated chain reactions processes, are associated with several types of biological damage. Sodium nitroprusside, a vasodilator drug induces oxidative brain injury, which is actually mediated by the hydroxyl radicals generated by iron element in sodium nitroprusside. Our defense system produces glutathione and other thiols which significantly reduce sodium nitroprusside and other reactive oxygen species. But for the neurodegenerative disorders, supplementation with external antioxidant agents is of need. Therefore much attention has been focused on the use of synthetic antioxidants to inhibit lipid peroxidation and to protect from damage due to free radicals[1] . Antioxidants play also an important role as corrosive inhibitor as they have the ability to inhibit oxidation process. There by leading to minimize oxygen which is considered one of the most corrosive agents removed by reductive inhibitors such as amines and hydrazines[2].

$O_2 + N_2H_2 \rightarrow 2\ H_2O + N_2$ In this example, hydrazine converts oxygen, a common corrosive agent, to water, which is generally benign. The problem of corrosion is common and occurs in various sectors, such as chemical industry, petrochemical, shipbuilding, construction, automotive, aviation, railway, maritime and others. The consequences of corrosion can result in economic loss, for example, the oxidation of residential pipes, vehicles and metal materials in general, but can also result in serious accidents, causing damage to both nature and man, for example, degradation in pipeline systems, bridge failures, and others[3, 4]. Coordination compounds possess high attention due to their structural variety, interesting physical & chemical properties and promising applications in many fields. Metal ions play an important role in the structure and function of many bio macromolecules and have important roles in the biological processes of metabolism as well as in pharmaceutical chemistry due to their chemical

properties. Compounds bearing carbonyl and thiocarbonyl groups are used as potential donor ligand for the preparation of complexes[5, 6]. Among these, thiourea and its derivatives are versatile ligands that coordinate to form stable compounds. They are able to coordinate with metal either as neutral or monoanion or dianion ligand[7]. These thiourea ligands and their metal complexes were reported to act as antioxidants, antimicrobial, antibacterial, antifungal, antimalarial, anti-tuberculosis, anticancer activities and anticorrosive agents. In view of the importance of thiourea and their derivatives it was important to synthesize N-substituted thiourea ligand and their complexes with transition metal elements because it was observed that this activity was enhanced by complexing with certain transition metal elements[7]. Complexes were synthesized using microwave-assisted irradiation. Microwave gives shorter reaction times, clean, high yields and low cost[7, 8]. A rapid, simple and inexpensive method to measure antioxidant activity is the use of the free radical, 2, 2-Diphenyl-1-picrylhydrazyl (DPPH) which is widely used to test the ability of compounds to act as free radical scavengers or hydrogen donors and to evaluate antioxidant activity[9]. The DPPH assay method is based on the reduction of DPPH, a stable free radical[10]. The free radical DPPH with an odd electron gives a maximum absorption at 517 nm (purple color). When Antioxidants react with DPPH, which is a stable free radical becomes paired off in the presence of a hydrogen donor (e.g., a free radical scavenging antioxidant) and is reduced to the DPPHH and as consequence the absorbance's decreased from the DPPH[11] Radical to the DPPH-H form, results in decolorization (yellow color) with respect to the number of electrons captured[12]. More the decolorization more is the reducing ability. This test has been the most accepted model for evaluating the free radical scavenging activity of any new drug[13]. When a solution of DPPH is mixed with that of a substance that can donate a hydrogen atom, it rises to the reduced form (Diphenylpicrylhydrazine; non radical) with the loss of this violet color (although there would be expected to be a residual pale yellow color from the picryl group still present)[14].

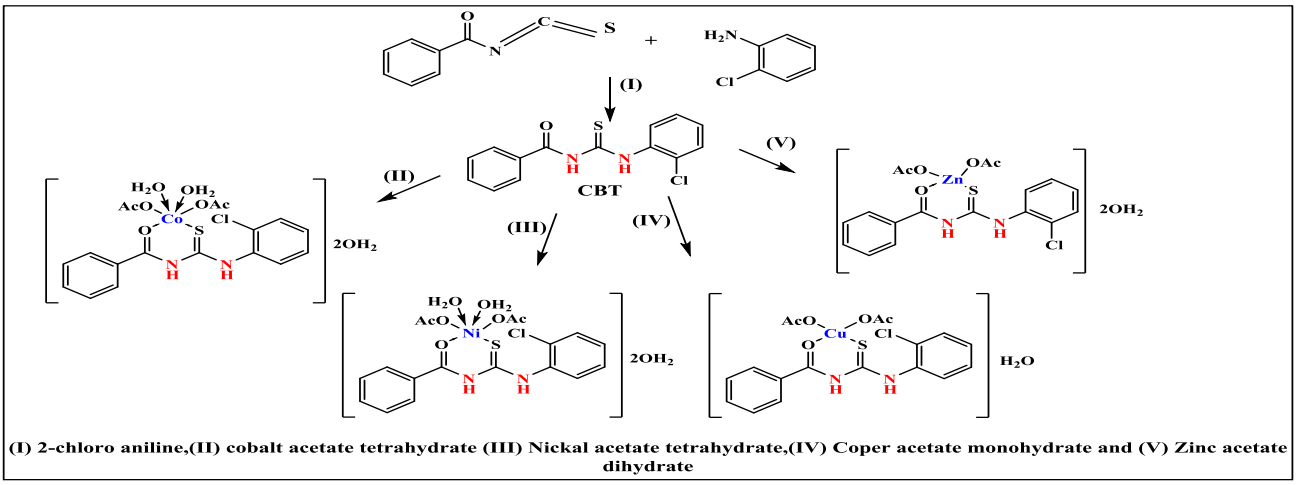
EXPERIMENTAL

Synthesis of ligands:

The two Ligands were prepared by reflux method between 0.1 m of ammonium thiocyanate in acetone and 0.1 m of benzoyl chloride to form Benzoyl thiocyanate. Then Benzoyl thiocyanate refluxed with ortho chloro analin and para chloro analin to form: N-*(2-chlorophenyl)-N'- benzoyl thiourea (CBT)* and *N-(4-chloro phenyl)-N'- benzoyl thiourea (PCBT)* respectively[19, 20].

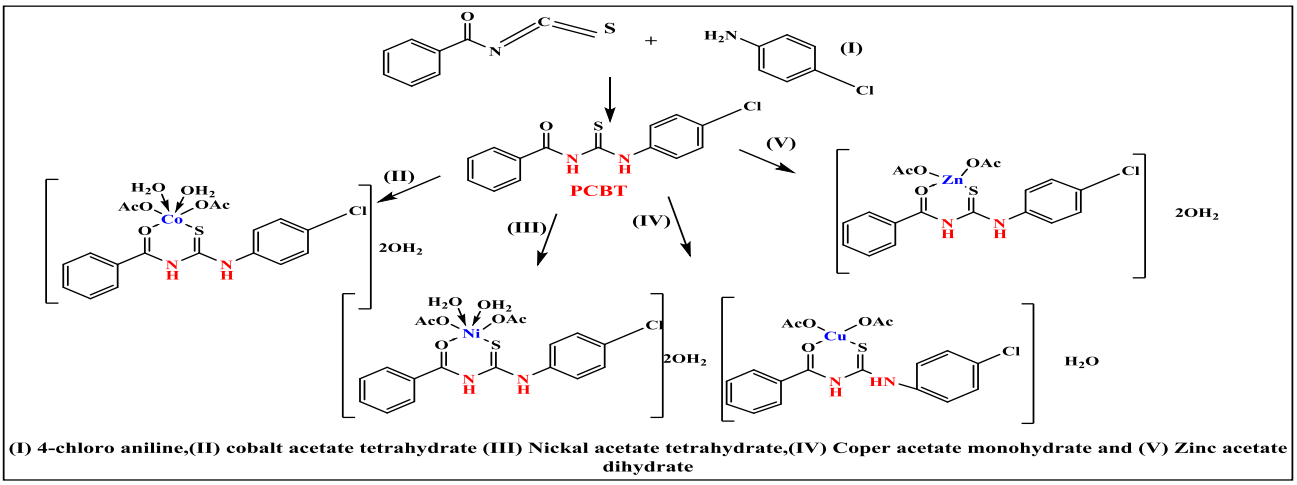
Synthesis of Metal Complexes

The prepared ligand and the acetate salts of the metals: Co $(CH_3COO)_2.4H_2O$, Ni $(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2.H_2O$ and Zn $(CH_3COO)_2.2H_2O$ were mixed in (1:1) ratio. Then irradiated in microwave for (3-5 min) to give the complexes with higher yields [19, 20]. Synthesis of N-(2-chlorophenyl)-N'-Benzoyl thiourea (CBT), *N-(4-chloro phenyl)-N'- benzoyl thiourea* (PCBT) and their metal complexes given in scheme 1 and 2.



(I) 2-chloro aniline,(II) cobalt acetate tetrahydrate (III) Nickal acetate tetrahydrate,(IV) Coper acetate monohydrate and (V) Zinc acetate dihydrate

Scheme-1: Synthesis of N-(2-chlorophenyl)-N'-Benzoyl thiourea (CBT) and its metal Complexes



(I) 4-chloro aniline,(II) cobalt acetate tetrahydrate (III) Nickal acetate tetrahydrate,(IV) Coper acetate monohydrate and (V) Zinc acetate dihydrate

Scheme-2: Synthesis of N-(p-chlorophenyl)-N'-Benzoyl thiourea (PCBT) and its metal Complexes

Evaluation of antioxidant activity by DPPH radical scavenging method:

Freshly prepared (0.004%w/v) methanol solution of 2, 2-diphenyl-1-picrylhydrazyl (DPPH) radical was prepared and stored at 10 ℃ in the dark. A DMSO solution of the test compound was prepared by dilution method[15]. The mixtures were then allowed to react in the dark for half an hour. Measurement of the mixture absorbance was achieved spectrophotometrically at 515 nm. Absorbance measurements were recorded immediately with a UV-visible spectrophotometer (UV-3101PC)[16]. The absorbance of the DPPH radical without antioxidant (control) and the reference compound ascorbic acid were also measured. All the determinations were performed in three replicates[17] and averaged. The percentage of the DPPH radical scavenging activity was calculated according to the equation: PI = [(AC- AS)/ AC) x 100].

Where: AC = Absorbance of the control [18]and AS = absorbance of the(sample +DPPH).

Corrosion Inhibition studies:

Corrosion inhibition behavior of the two synthesized ligands (CBT) and (PCBT) was evaluated on carbon steel coupons by using weight loss measurements as follows:

The surface of the carbon steel coupons was abraded successively by different grade of metallographic emery papers until the surface appears free from any scratches and other apparent defects, then degreased with hot acetone, washed with distilled water and finally dried at room temperature. Tests were conducted on carbon steel coupons of the following composition: (0.11%C, 0.45% Mn, 0.04% P, 0.05% S, 0.25% Si, and the remained is Fe). The concentrations of the prepared ligands were 0.5 × 10−4 M, 0.75 × 10−4M, 2.5 × 10−4 M, 5 × 10−4 M, and 7.5 × 10−4 M. All solutions were prepared using distilled water. The experiments were carried out using carbon steel coupons immersed in 1.0 M HCl solution in absence and presence of different concentrations of the two synthesized ligands. Tests were conducted under total immersion conditions in 100 ml of the aerated test solutions. To determine weight loss with respect to time, test coupons were retrieved after 24 h immersion time, scrubbed with a bristle brush, washed, dried, and reweighed. The weight loss was taken as the difference between the initial and final weights of the coupons. Weight loss measurements were done at 30 °C.

RESULTS AND DISCUSSION

Mass spectroscopy:

The mass spectra of CBT (Fig.1) (Scheme 3) show multi peak representing successive degradation of the ligand. The spectra show the peak m/e = 292.74 represent the molecular ion peak ($C_{14}H_{11}ON_2SCl$) with 39.57% abundance. The base peak 100% with m/e =145.79.

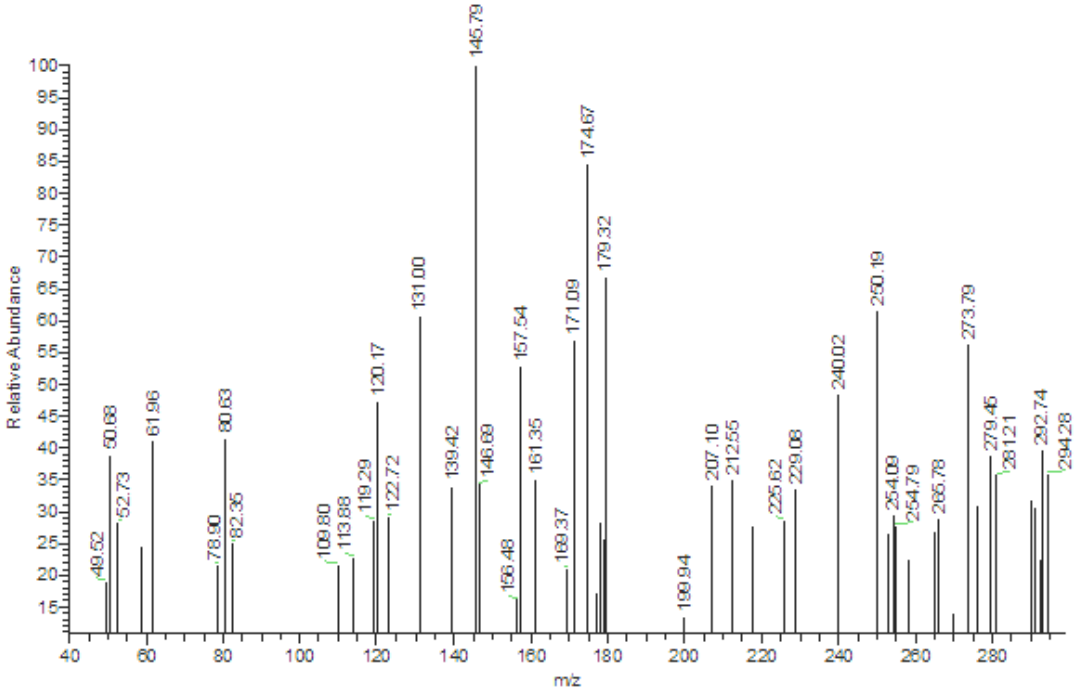
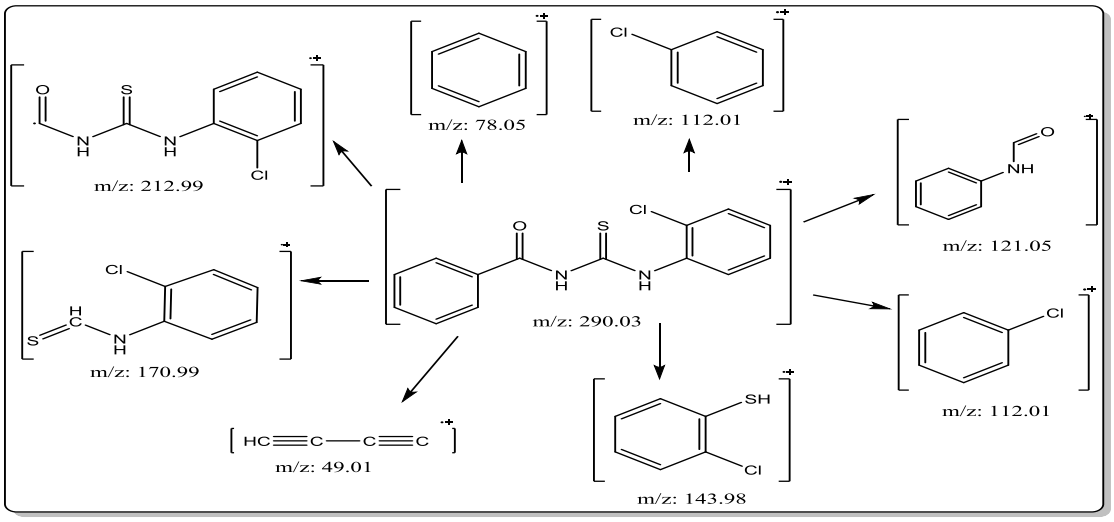


Figure-1: Mass spectra of the prepared ligand (CBT)



Scheme3: Suggested mass fragmentation patterns of the prepared ligand (CBT)

The mass spectra of PCBT (Fig.2) (Scheme 4) show multi peak representing successive degradation of the ligand. The spectra show the peak m/e = 290.77 represent the molecular ion peak ($C_{14}H_{11}ON_2SCl$) with 52.7% abundance. The base peak 100% with m/e =106.06.

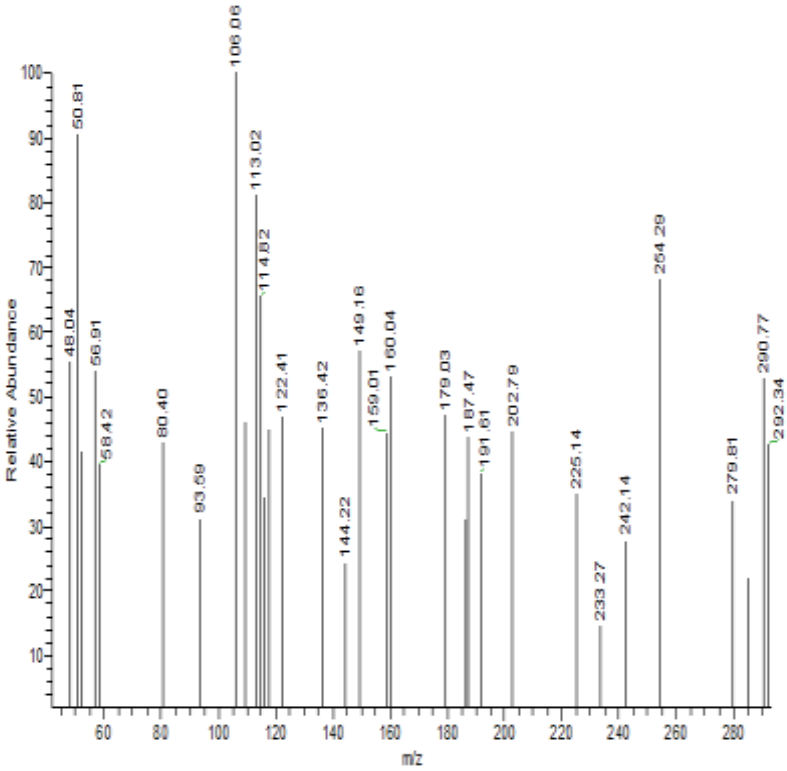
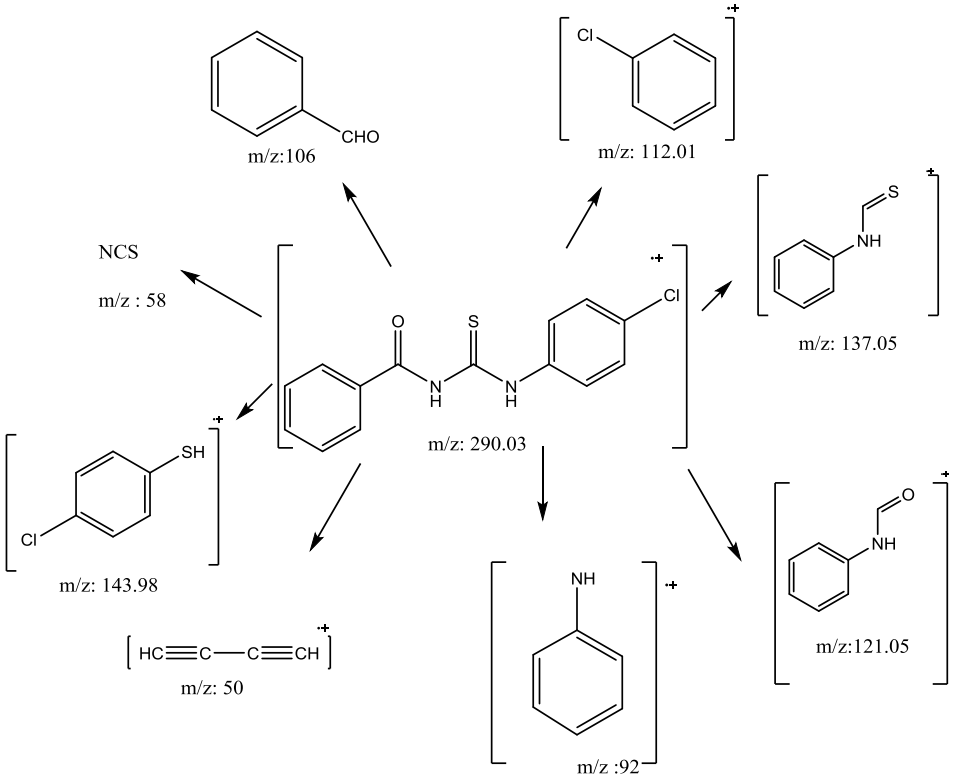


Figure-2: Mass spectra of the prepared ligand (PCBT)



Scheme4: Suggested mass fragmentation patterns of the prepared ligand (PCBT)

The mass spectra of Zn-CBT (Fig.3) (Scheme: 5) show multi peak representing successive degradation of the ligand. The spectra show the peak m/e = 510.94 represent the molecular ion peak ($C_{18}H_{21}O7N_2SCl$) with 21.06% abundance. The base peak 100% with m/e =52.62.

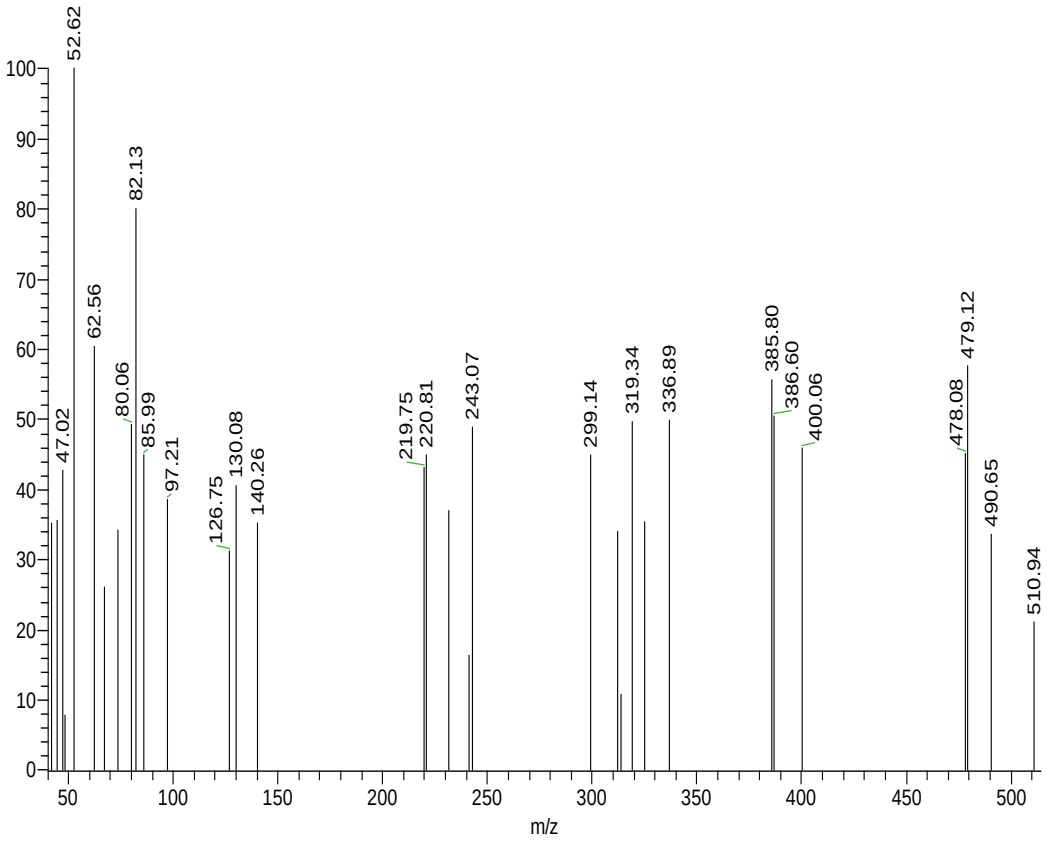
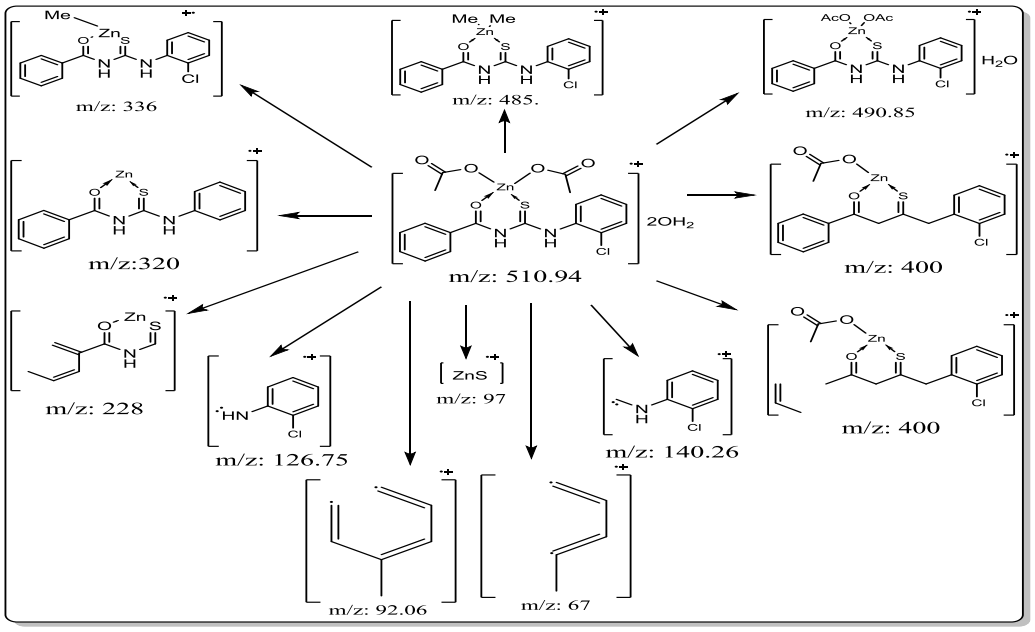


Figure-3: Mass spectra of the prepared Zn^{II} complex of CBT



Scheme 5: Suggested mass fragmentation patterns of the prepared Zn complex of **CBT**

The mass spectra of Co-PCBT (Fig.4) (Scheme: 6) show multi peak representing successive degradation of the ligand. The spectra show the peak m/e = 539.33 represent the molecular ion peak ($C_{18}H_{25}O9N_2SCl$) with 22.52% abundance. The base peak 100% with m/e =316.6.

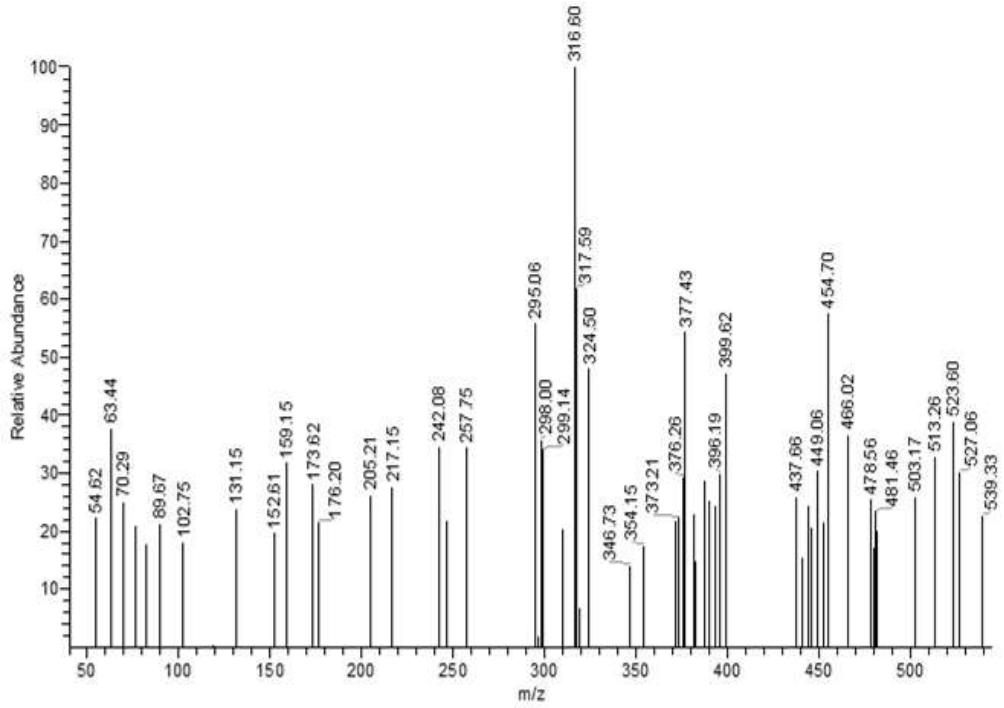
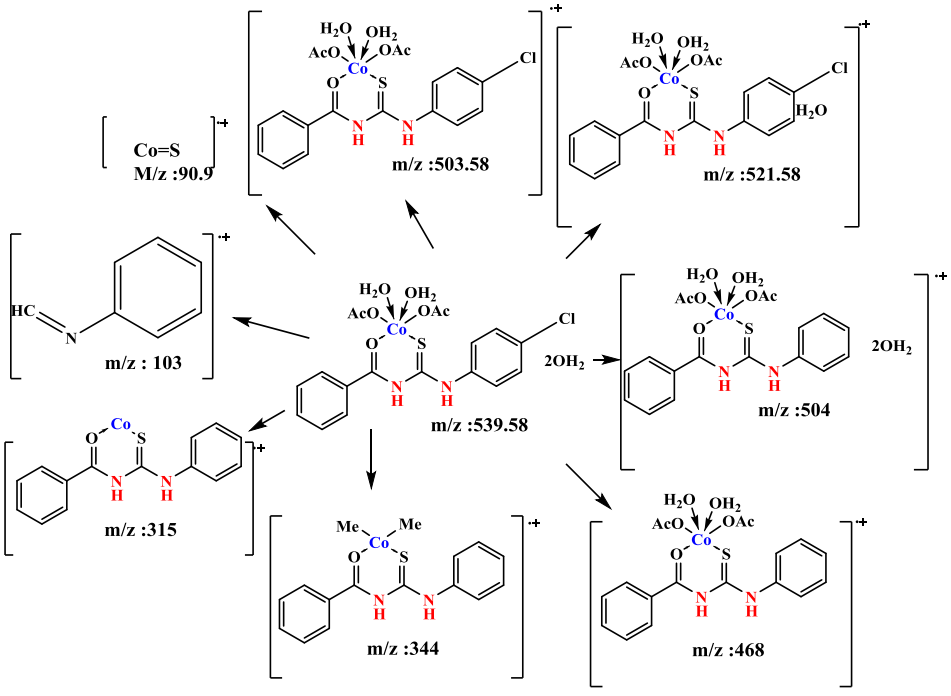


Figure-4: Mass spectra of the prepared Co^{II} complex of PCBT



Scheme 6: Suggested mass fragmentation patterns of the prepared Co (II) complex of PCBT

H^1NMR Spectroscopy:

For the ligand (CBT) fig.5 give two singlet signals, one at δ 11.78 ppm assigned to (S,1H, N8-H) and the other at δ 12.742 ppm assigned to(S,1H, N10-H) [22] (which were also identified by D_2O exchange) . The multiplets observed at δ 7.293 – 8.098 ppm are attributed to the phenyl protons.

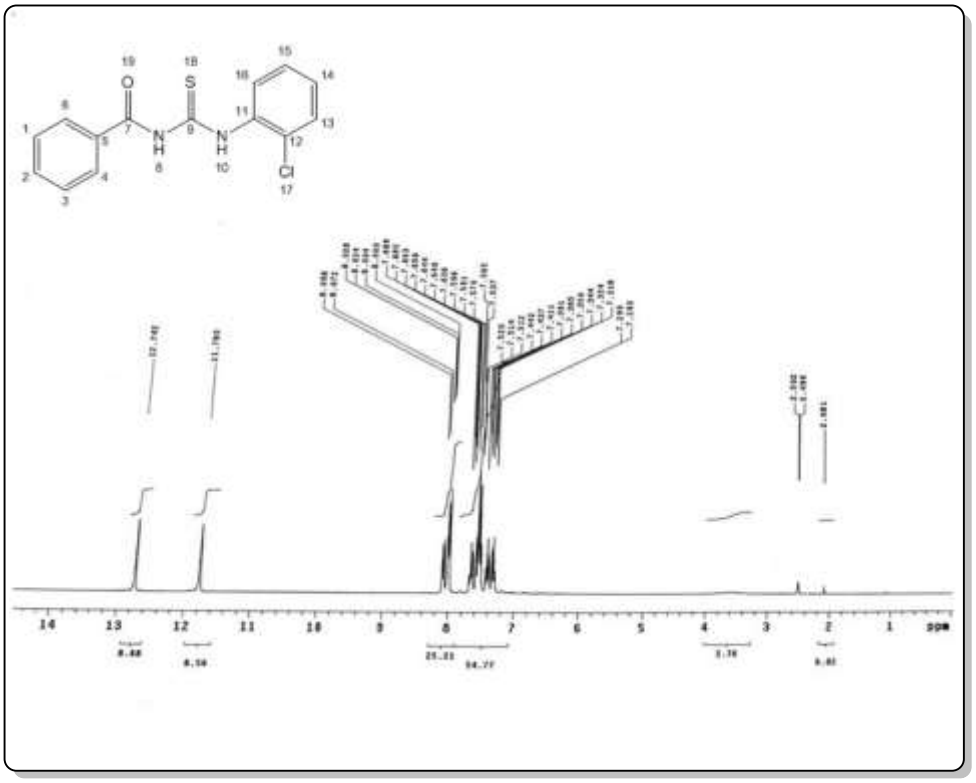


Figure-5: 1H NMR spectra of the ligand (CBT)

For ligand (PCBT) fig. 6 give two singlet signals, one at δ 11.58ppm assigned to (S,1H, N8-H) and the other at δ 12.59 ppm assigned to(S,1H, N10-H) [22] (which were also identified by D_2O exchange) . The multiplets observed at δ 7.450 – 8.000 ppm are attributed to the phenyl protons.

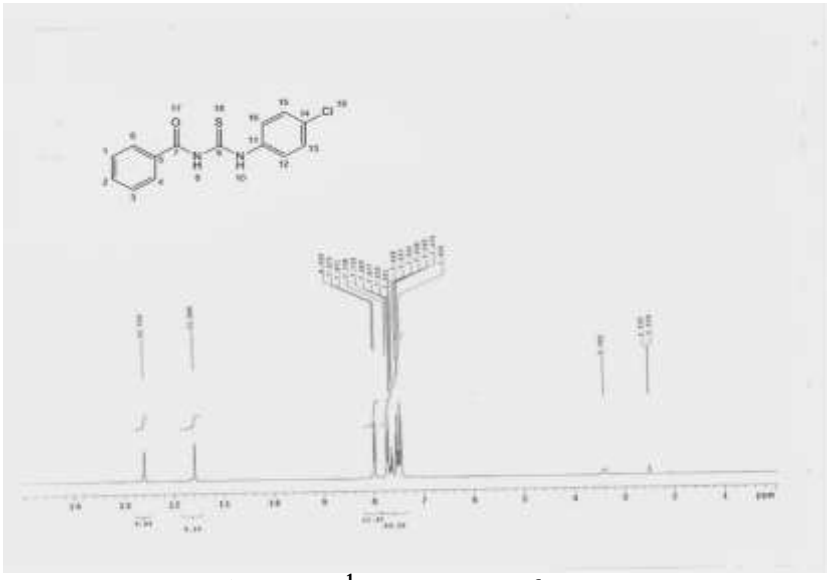


Figure-6: H^1NMR Spectra of PCBT

^{13}CNMR spectroscopy:

The ^{13}CNMR spectra of the synthesized ligand (CBT) fig.7 showed peaks at 180.219 ppm assigned to (C=O), 168.556 ppm assigned to (C=s), 135.357 ppm (C11) 133.239 ppm(C16), 131.858 ppm, (C5) ,129.483ppm(C2) and at 128.793 ppm(C12), 128.261 ppm(C13), 128.110 ppm(C1 and C3), 126.167 ppm (C4 and C6).

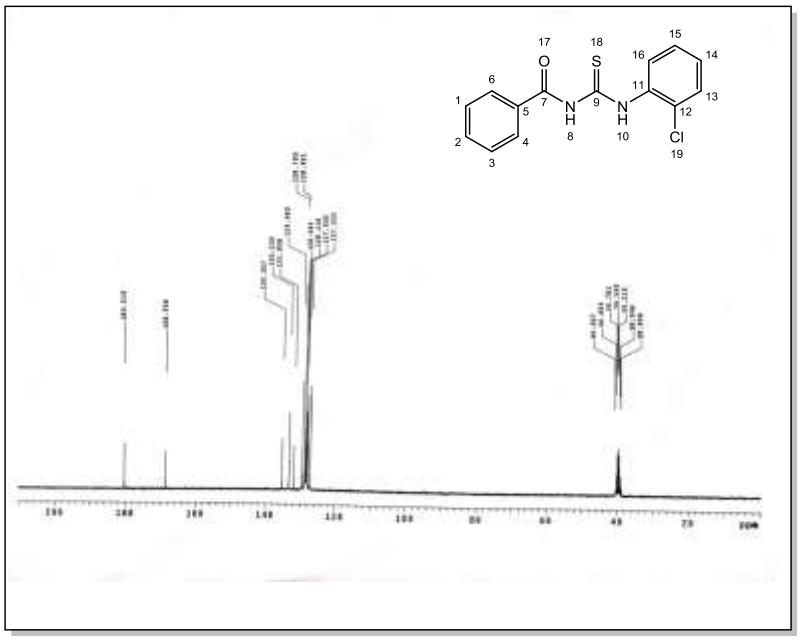


Figure-7: 13C NMR spectra of the ligand (CBT)

The ^{13}CNMR spectra of the synthesized ligand (PCBT) fig.8 showed peaks at 179.347 ppm assigned to (C=O), 168.207 ppm assigned to (C=S), 136.958 ppm to (C11) 133.133 ppm to (C14), 132.63 ppm to (C5), 130.257 ppm to (C2) ,130.257 ppm to (C12 , C16) and at 128.694 ppm(C13,C15), 128.550 ppm (C1,C3), 126.167 ppm(C4 and C6).

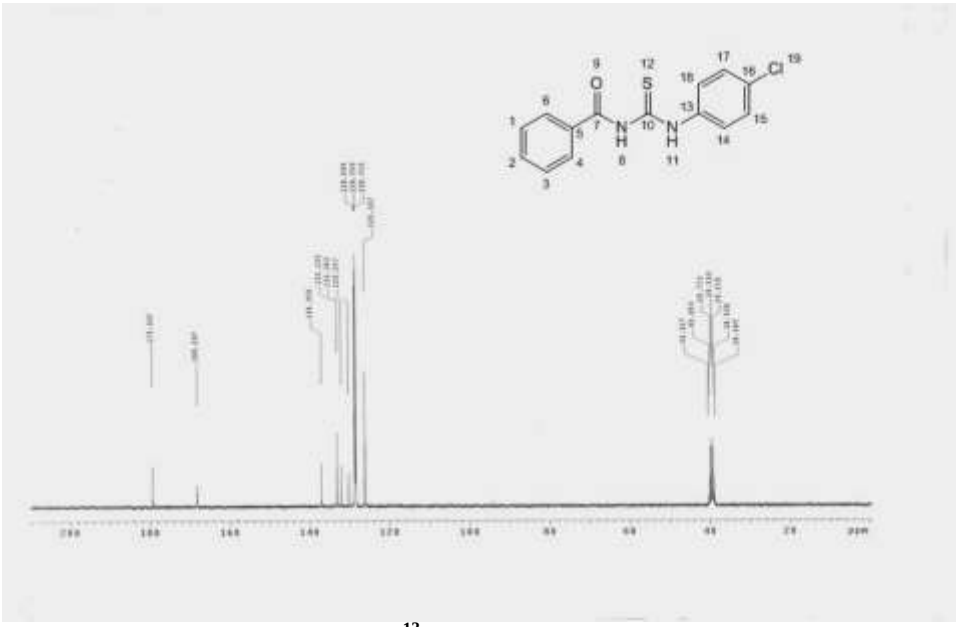


Figure-8: C^{13}NMR Spectra of PCBT

IR spectra:

The characteristic IR bands of the thiourea ligands showed the expected frequencies of υ (C=O), υ (N-H), υ (C-N) and υ (C=S) and upon coordination of the metal center to ligand, these characteristic bands were found to be shifted to a lower frequency. This finding may be taken as an evidence for the coordination of the carbonyl oxygen and thionyl Sulphur atoms with the metal. The IR data of ligands and complexes are tabulated in Table1 and 2 [19, 20].

Table 1:I.R bands of the synthesized ligand CBT and its complexes

Cpd.	υ OH (H2O)	υ N-H	υ C-H Aromatic	υ OAc Assym. /Sym.	υ C=O	υ C=S	υPh-Cl	υ M-O	υ M-S
CBT	--	3312	3018	--	1669	1329	753	--	--
CBT-Co	3850	3310	3016	1435	1666	1249	679	594	540
CBT-Ni	3700	3309	3016	1427	1666	1242	678	594	509
CBT-Cu	3850	3371	3016	1442	1597	1242	694	578	532
CBT-Zn	3448	3209	3008	1404	1601	1288	686	617	501

Table 2:I.R bands of the synthesized ligand PCBT and its complexes

Cpd.	υ OH (H2O)	υ N-H	υ C-H Aromatic	υ OAc Assym. /Sym.	υ C=O	υ C=S	υPh-Cl	υ M-O	υ M-S
PCBT	--	3251	3020	--	1670	1341	765	--	--
PCBT-Co	3742	3348	3148	1396	1550	1273	679	609	501
PCBT-Ni	3850	3441	2993	1412	1535	1250	686	609	509
PCBT-Cu	3700	3487	3148	1442	1605	1273	694	625	501
PCBT-Zn	3850	3464	3009	1342	1535	1250	686	609	501

Electronic and magnetic properties of the prepared compounds

The stereochemistry of the metal ions in the complexes can be assigned via the electronic spectral measurements. The spectra of the ligands and there complexes in solid-state showed a number of bands in the UV -Vis region (200-800 nm) table 3, 4 [19, 20].

Table-3: Electronic Spectra, magnetic for CBT metal complex

Cpd	λ_{max}, nm	Assignments	$\mu_{eff.}$(B.M)	*Suggested Structure*
CBT	330 290 260	(n-π*, C=O), (n –π*, C=N), (π –π*, aromatic ring)	--	-
CBT-Co	425-650	4T1g (F) →4T1g(P) 4T1g (F)→4T2g	5.8	Octahedral
CBT-Ni	450-750	$^3A_2g \rightarrow {}^3T_1g$ (P) $^3A_2g \rightarrow {}^3T_2g$	2.9	Octahedral
CBT-Cu	425-750	2B2 → 2E	1.78	Tetrahedral
CBT-Zn	560-720	MLCT	Di	Tetrahedral

Table-4: Electronic Spectra, magnetic for PCBT metal complex

Cpd	λ_{max}, nm	Assignments	$\mu_{eff.}$(B.M)	*Suggested Structure*
pCBT	325 277 258	(n-π*, C=O), (n –π*, C=N), (π –π*, aromatic ring)	--	-
PCBT-Co	425-650	4T1g (F) →4T1g(P) 4T1g (F)→4T2g	5.95	Octahedral
PCBT-Ni	450-750	$^3A_2g \rightarrow {}^3T_1g$ (P) $^3A_2g \rightarrow {}^3T_2g$	3.9	Octahedral
PCBT-Cu	425-750	2B2 → 2E	1.89	Tetrahedral
PCBT-Zn	560-720	MLCT	Di	Tetrahedral

Measurement of Antioxidant activity:

The percentage of the DPPH radical scavenging activity of CBT and its Zn^{II} complex was calculated and the results was tabulated in table 5 and expressed in figure 9.

Table-5: The percentage of the DPPH radical scavenging activity of CBT and its Zn^{II} complex

Sample concentration (µg/ml)	DPPH scavenging %(CBT)	DPPH scavenging %(CBT-Zn)
1440	**78.90**	**4.09**
720	**70.77**	**3.47**
360	**66.26**	**1.01**
180	**35.03**	**0.62**
90	**34.96**	**0.44**
45	**34.81**	**0.34**
22.5	**31.24**	**0. 16**
0	**0**	**0**

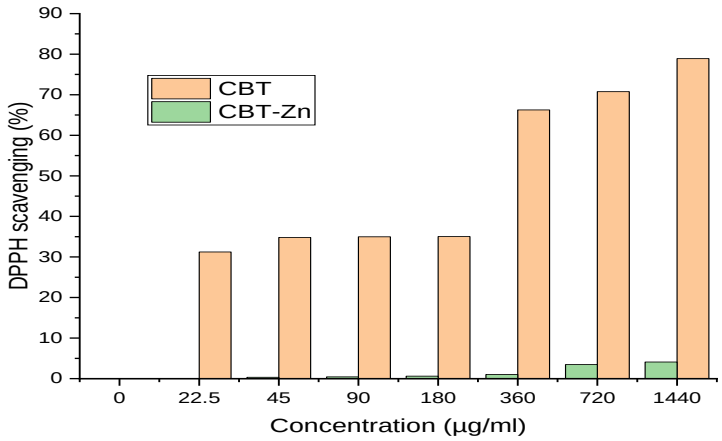


Figure-9: The DPPH radical scavenging activity of CBT and its Zn^{II} complex

The percentage of the DPPH radical scavenging activity of PCBT and its Co^{II} complex was calculated and the results was tabulated in table 6 and expressed in figure 10.

Table-6: The percentage of the DPPH radical scavenging activity of PCBT and its Co^{II} complex

Sample concentration (µg/ml)	DPPH scavenging %(PCBT)	DPPH scavenging %(PCBT-Co)
1440	58.49	23.01
720	55.39	18.63
360	53.81	16.76
180	53.73	7.83
90	50.69	3.59
45	45.39	1.97
22.5	16.28	0.35
0	0	0

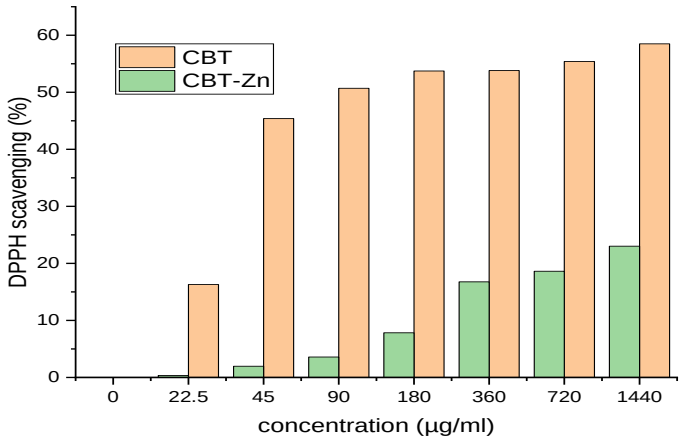


Figure-10: The DPPH radical scavenging activity of PCBT and its Co^{II} complex

For comparison purpose, the effect of ascorbic acid as standard antioxidant was evaluated and produced (IC_{50} ml) under the same conditions table 7 and figure 11.

Table-7: The percentage of the DPPH radical scavenging activity of Ascorbic acid

Sample conc. (µg)	DPPH scavenging %
30	80.10
25	76.99
20	70.84
15	54.70
10	16.50
5	11.76
0	0

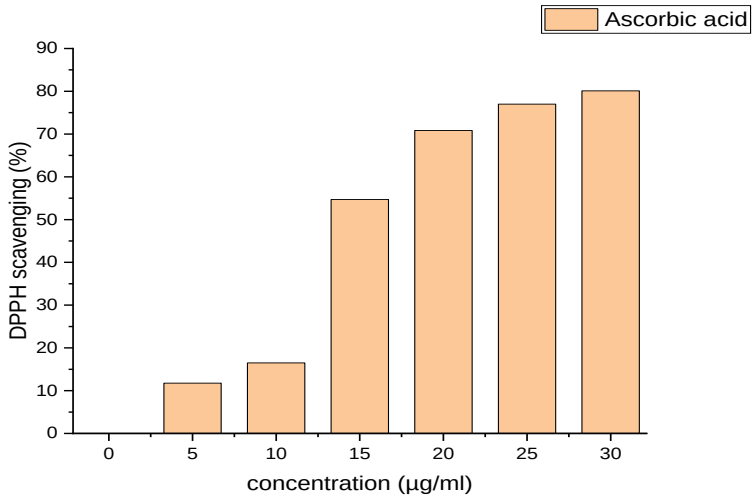


Figure-11: DPPH radical scavenging activity of Ascorbic acid

The reported results in terms of IC_{50} value was recorded in table 8

Table 8: IC_{50} values of Ascorbic acid and compounds under study

Compound	**IC_{50} (µg/mL)**
Ascorbic Acid	14.4
CBT	250
PCBT	84
CBT-Zn	-
PCBT-Co	-

Corrosion Inhibition Measurements:

Table 5 shows the calculated values of corrosion rate (mg cm^{-2} h^{-1}), inhibition efficiency (η_w %) and the degree of surface coverage (θ) for steel dissolution in 1.0 M HCl in the absence and presence of the surfactants under study. The values of corrosion rate were calculated from the following equation:

$$K=\Delta W / At$$

Where k is the corrosion rate (mg cm^{-2} h^{-1}), ΔW is the loss of weight after corrosion (mg), A is the total area of the coupon (cm^2), and t is the corrosion time (h). The degree of surface coverage (θ) and the inhibition efficiency, η_w%, were calculated using the following equations[21]:

$$\theta = \frac{K_0 - K}{K_0}$$

$$\eta\% = \frac{K_0 - K}{K_0} \times 100$$

Where k_o and k are the values of the corrosion rate without and with addition of the inhibitor, respectively. From Table 9 we can find that:

For PCBT the inhibition efficiency percentage (η_w%) increases with increasing inhibitor concentration, which is due to the increase in the mass and charge transfer to the carbon steel surface leading to the adsorption of inhibitor molecules and reducing the metal dissolution. Also, more surface area (θ) is covered by increasing inhibitor concentration.

For the CBT it was found that the corrosion rate increases by increase the concentration and so the inhibition efficiency percentage and surface area decreases by increase the concentration. This can be explained by that the chloride in the ortho position have more electron withdrawal effect than the para position in PCBT this leads to decrease the charge transfer to the carbon steel surface which leads to increase corrosion.

Table-9: Weight loss data for steel 1.0 M HCl without and with different concentrations of the ligands

Inhibitor name	Conc.(M)	k (mg cm-2 h-1)	Θ	ηw%
Blank	0×10^{-4}	1.5916	-----	-----
CBT	0.5×10^{-4}	1.5916	0	0
	0.75×10^{-4}	1.75	-0.15	-15
	2.5×10^{-4}	1.84	-0.248	-24.8
	5×10^{-4}	2.083	-0.3225	-32.25
	7.5×10^{-4}	2.173	-0.4914	-49.14
PCBT	0.5×10^{-4}	1.563	0.0177	1.77
	0.75×10^{-4}	1.24	0.2199	21.99
	2.5×10^{-4}	0.74	0.535	53.5
	5×10^{-4}	0.705	0.557	55.7
	10×10^{-4}	0.5	0.6858	68.58

Adsorption Isotherm

According to corrosion studies it is important to know the relationship between the inhibitor molecules and the surface of the metal which obtained by the adsorption of these molecules on the metal surface by two different types of adsorption. Generally, adsorption of an inhibitor maybe classified as a physical adsorption and chemisorption. The main factors affecting the adsorption type are the electronic structure of the metal, the type of electrolyte and the chemical structure of the inhibitor. Furthermore, adsorption process take place when the water molecules ($H_2O_{(ads)}$) which were previously adsorbed on the metal surface are replaced by the inhibitor molecules ($Inh_{(sol)}$) present in the aqueous solution as follows:

$$Org_{(sol)} + x\ H_2O_{(ads)} \rightarrow Org_{(ads)} + x\ H_2O_{(sol)}$$

Where x is the size ratio representing the number of water molecules replaced by one organic molecule. Different adsorption isotherm equations such as Freundlich, Langmuir, Frumkin, Flory-Huggins, Frumkin and Temkin can be applied to the resulted data resulted, but it was found that the data are more likely to fit with the Langmuir isotherm especially when the correlation coefficients (R^2) for CBT and PCBT are 0.8119 and 0.0535 respectively figure 12 and 13. The Langmuir relation is as follow:

$$\text{Langmuir Isotherm} = C_{inh} / \theta = 1 / k_{ads} + C_{inh}$$

Where C_{inh} is the inhibitor concentration; K_{ads} is the equilibrium constant of the isotherm process and θ is the degree of surface coverage. By plotting C_{inh}/θ versus C, it was found that the slope of Langmuir adsorption isotherm for the three synthesized inhibitor **PCBT** at 30 °C was almost close to unity except a slight deviation took place which may be referred to the interaction between the adsorbed inhibitor molecules with each other[22, 23].Values of the equilibrium constant (K_{ads}) for inhibitor **PCBT** were 3.376×10^3, 45.88×10^3 and 0.726×10^3 respectively , these values indicates how strong the adsorption force between the synthesized inhibitors and the surface of the metal. It is also known that the equilibrium constant (K_{ads}) is related to the Gibbs free energy according to the equation [24]:

$$\Delta G^{\circ}_{ads} = -RT \ln (55.5\ K_{ads})$$

Where (55.5) is the molar concentration of water in solution expressed in mole/l, *R (8.314)* is the universal gas constant and *T* is the absolute temperature. Generally, when ΔG°_{ads} values are equal to -20 or higher it may be considered as (Physical adsorption), while values of -40 or lower are of the type (chemisorption)[25]. Calculated values of the Gibbs free energy for inhibitors **MBT** and **PCBT** were –30.58834 and - 26.7168 KJ mol^{-1} as tabulated in Table 10. So it is obvious that this values indicating that the adsorption processes were of chemically adsorption type on the surface of the carbon steel that also indicating an electron transfer process took place to form a coordination bond between the inhibitor molecules and the d-orbital of the iron molecules[26, 27].

Table-10: Thermodynamic parameters using Langmuir adsorption isotherm on steel surface in 1.0 M HCl containing different concentrations of the ligands MBT and PCBT

Inhibitor	Temp. (°k)	K_{ads} (KJ/mol)	ΔG_{ads} (KJ/mol)	ΔS_{ads} (J/mol .°k)	ΔH_{ads} (KJ/mol)
MBT	303	3376.074458	-30.58834	0.304748049	61.75
PCBT	303	726.2650946	-26.7168	0.500414166	124.91

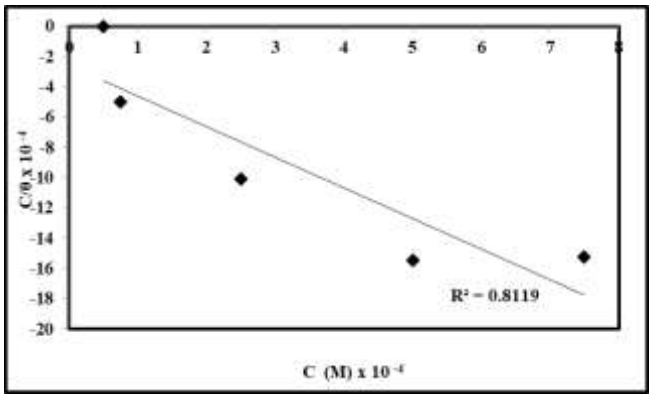


Figure-12: Langmuir isotherm adsorption model on the carbon steel surface of Schiff base inhibitor CBT in 1.0 M HCl at 30 °C

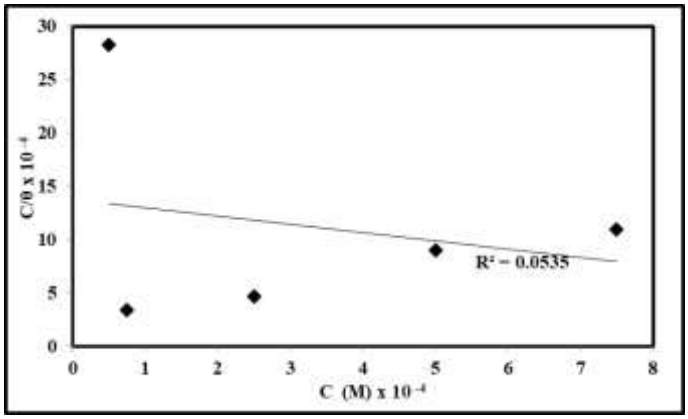


Figure-13: Langmuir isotherm adsorption model on the carbon steel surface of Schiff base inhibitor PCBT in 1.0 M HCl at 30 °C

Enthalpy (ΔH_{ads}) and Entropy (ΔS_{ads}) of Adsorption:

Enthalpy and Entropy of adsorption can be calculated as follows:

$$ln\ K_{ads} = \left(\frac{\Delta H_{ads}}{RT}\right) + const$$

$$\Delta G = \Delta H_{ads} - T\Delta S_{ads}$$

Where ΔH_{ads} and K_{ads} are the adsorption heat and adsorptive equilibrium constant, respectively. Plotting ln K_{ads} against $1/T$ gives straight link which slope is equal to ΔH_{ads} /R. Negative values of ΔH_{ads} are shown in Table 10 indicating that the adsorption of inhibitors is exothermic in nature. Also, the negative values of ΔH_{ads} show that the adsorption is exothermal with an ordered phenomenon ascribed by the negative values of ΔS_{ads}. This order may more probably be explained by the possibility of formation of iron complex on the metal surface [28, 29].

CONCLUSION

DMSO solution of the compounds under study showed good antioxidant potential by DPPH radical scavenging method when compared to standard ascorbic acid and IC_{50} value found to be 14.4 µg/ml for ascorbic acid, 250 µg/ml for CBT and 84 4 µg/ml for PCBT where the complexes show low activity . And then by study the anticorrosion activity of ligands CBT and PCBT showed that: PCBT has good inhibition efficiency as inhibitor for carbon steel dissolution in 1.0 M HCl solution, but CBT cannot be used as corrosion inhibitor.

So, it can be said that some of thiourea derivatives can be useful for man health as antioxidants and economy as anticorrosive agents.

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