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Anticancer and Antioxidant Activities of Biologically Active Newly Synthesized α-Amino Acid-Dithiocarbamate Complexes of Some Bivalent Metals

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The present study focuses on the synthesis and characterization of L-proline dithiocarbamate and its L-prodtc metal(II) (M = Ni^{2+}, Cu^{2+} and Se^{2+}) complexes. The ligand was synthesized in the presence of an alkali through the reaction of one mole of carbon disulphide and L-proline in ethanol under ice cold condition. The solubility of this ligand in the media is attributed to its high hygroscopic character and therefore, its metal(II) complexes were synthesized using a freshly prepared ligand. The characterization of the metal(II) complexes were carried out by molar conductance, magnetic susceptibility, elemental analysis, TGA/DTA, mass, IR, Raman, UV-Visible, ^1H and ^{13}C NMR spectroscopic studies. The biological activity of all the metal(II) complexes has been examined using an inhibition method for bacteria and pathogenic fungus, which will assess their possible antibacterial, antioxidant, anticancer activities and anti-inflammatory. It has been observed that $Se(L\text{-}Prodtc)_2$ exhibits anticancer activity against breast cancer cells (MCF7) and also observed that antioxidant activity of $Se(L\text{-}Prodtc)_2$ is more as compared to standard BHT, whereas $Cu(L\text{-}Prodtc)_2$ complex shows appreciable anti-inflammatory activity.

Keywords: Dithiocarbamate, Metal(II) complexes, L-Proline, Raman Antioxidant, Antimicrobial agent.

INTRODUCTION

Due to the structural properties of metal dithiocarbamate complexes that enable chelation to the metal center render them interesting for preparation, characterization and application [1-3]. Several reviews have been devoted upon the synthesis, characterization and application of dithiocarbamate metal complexes. The extensive utilization of dithiocarbamates (DTC) as insecticides and fungicides can be attributed to its distinctive structural formula [$R_2N\text{-}C(=S)\text{-}S\text{-}R$]. Recently, they have also found applications as vulcanization accelerators in the rubber industry, owing to their strong ability to form chelates with inorganic species. It is interesting to explore the nature of the dithiocarbamates derived from α-amino acids and its metal complexation [4-7].

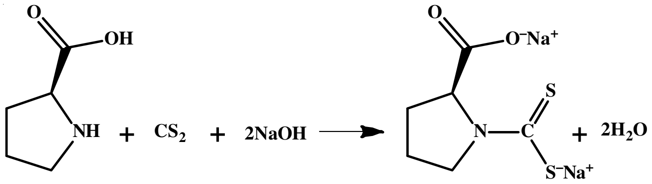
Dithiocarbamate exhibits significant utility in various biological contexts due to its ability to coordinate with metal ions in monodentate, bidentate and tridentate ligand topologies [8,9]. Moreover, the oxygen bonding capability of the conjugates generated by dithiocarbamates also makes them helpful to metals with a changeable oxidation state since they are stable with these metals in all oxidation states [10,11]. In present study, the synthesis and characterization of bivalent nickel, copper, zinc and selenium L-prolinedithiocarbamate complexes and their biological potential (*in vitro*) as antibacterial, antioxidant and cytotoxic agents were carried out.

EXPERIMENTAL

Metal(II) salts such as copper sulphate, nickel sulphate and selenium oxide received from Loba Chemicals, India were used as such. The elemental analysis and the spectral analysis were performed at Department of Chemistry and SAIF IITM, Chennai, India, respectively.

Characterization: The conductance values of the synthesized metal(II) complexes were measured with Precision conductivity bridge model WER/JAV NTW, WEST Germany. The magnetic properties were determined by VSM Lake Shore 7410, whereas the powder XRD data were collected between 5-100º 2θ range using D8 Advance (Bruker) instrument. The morphology of the compounds was characterized using SEM images, which were obtained through FEI Quanta-200MK II instrument. The IR spectrum were recorded in the range 4000-500 cm^{-1} using BRUKER-ALPHA-Platinum-ATR IR, while the Raman spectrum was measured in Bruker RFS 27. Bruker AVIII 500 MHz spectrometer was used to record ^{1}H and ^{13}C NMR spectra in MeOD, whereas the ESI-mass spectrum was recorded from a Q-Tof-mass spectrometer. The ultraviolet-visible spectrum was recorded from Perkin-Elmer LAMBDA 950UV-VIS-NIR spectrophotometer. The thermal behaviour of the metal(II) complexes were analyzed from TGAQ 500 HI-RES Instrument.

Synthesis of L-proline dithiocarbamate ligand: The ligand was synthesized according to the reported method [2]. In brief, 50 mL of ethanolic solution of L-proline (0.1 mol, 11.53 g) was mixed with NaOH (0.2 mol, 8 g) at < 4 ºC for the duration of the process under atmospheric pressure followed by the addition of carbon disulphide (0.1 mol, 7.8mL) mixed with 25mL of ethanol in a dropwise manner with magnetically constant stirring the solution for another 0.5 h. Using excess acetone, a small quantity of Na_2(L-Prodtc) as precipitates as a white salt (**Scheme-I**). This precipitate has the ability to absorb water, causing it to transform into a viscous liquid. To synthesize metal(II) (Ni^{2+}, Cu^{2+} and Se^{2+}) complexes, a solution of Na_2(L-Prodtc) was utilized.



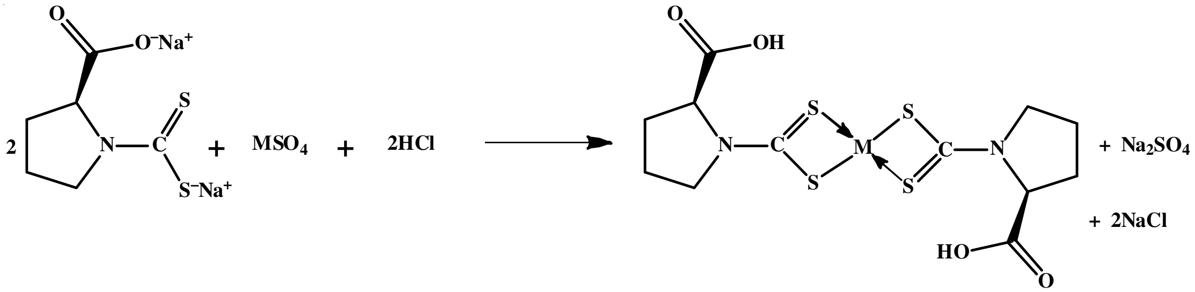
Scheme-I: Reaction pathway of Na_2 (L-prolinedithiocarbanate) ligand

Synthesis of M(II) L-prolinedithiocarbamate (Ni^{2+}, Cu^{2+} and Se^{2+}) complexes (1-3): The synthesis of metal(II) complexes **1**, **2** and **3** were carried out by a two step process following the methods reported in the research work [2]. The metal solution of $CuSO_4·5H_2O$ (1 mmol, 0.19965 g), $NiSO_4·6H_2O$ (1 mmol, 0.24968 g) and SeO_2 (0.11096 g) were prepared and added to the ligand (5 mmol) in the proportion of M:L/ML$_2$. A dark-brown, light-green and light-yellow coloured solid were precipitated for bivalent copper, nickel and selenium L-prolinedithiocarbamate, respectively. The precipitates were allowed to stand for 1 h, filtered, washed and recrystallized from methanol and dried in a desiccator [12,13]. The synthetic route the prepared complexes **1**, **2** is depicted in **Scheme-II**, whereas for complex **3** is shown in **Scheme-III**.

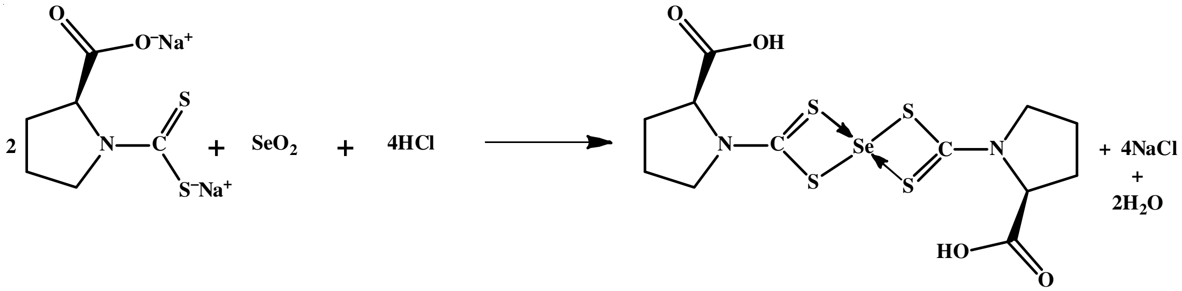
Biological studies: The synthesized metal(II) compounds were evaluated for their antimicrobial activity like antibacterial, antifungal activity by agar diffusion assay [14] for different concentration of the sample solutions, the results were compared to a known positive control. Further in the aim of exploring the biological applications the sample were put through anti-inflammatory studies, cytotoxicity, the ability of inhibition of oxidation and anticancer property were determined by standard methods [15-18].

RESULTS AND DISCUSSION

The structure of metal(II) complexes was determined using IR, ^{1}H & ^{13}C NMR spectra, elemental analysis and magnetic susceptibility studies. The complexes exhibit vibrant colours and are highly stable solid at room temperature. The low molar conductance values of all the metal(II) complexes indicate that they are non-electrolytic in nature. The elemental analysis results (Table-1) of the L-proline dithiocarbamate complexes are in excellent accordance with the calculated values for the proposed formula, confirming a 1:2 ratio of metal to ligand stoichiometry in all the complexes. The pattern of four-fold coordination in confirmed from the results obtained. Mass spectrum were recorded for the complexes **1-3**. The complexes were 90% pure when tested by TLC method. ESI mass spectra show a peak at 437 (*m/z*), for Cu (L-Prodtc)$_2$, for Ni(L-Prodtc)$_2$ a peak at 437 (*m/z*) and a peak at 466 (*m/z*) for Se(L-Prodtc)$_2$, respectively.



Scheme-II: Reaction pathway of complex Cu(II)L-Prodtc and Ni(II)L-Prodtc complexes (MSO_4 = $CuSO_4$, $NiSO_4$)



Scheme-III: Reaction pathway of bivalent selenium (L-prodithiocarbamate) complex

TABLE-1
PHYSICO-ANALYTICAL ANALYSIS OF SYNTHESIZED COMPLEXES **1-3** OF L-PROLINE DITHIOCARBAMATE

Complex	m.f.	Yield (%)	Colour	m.w. (g/mol)	Elemental analysis (%): Observed (expected)				
					C	H	N	S	M
1	$C_{12}H_{16}N_2S_4O_4Cu$	67	Dark brown	443	32.02 (32.5)	3.52 (3.6)	6.41 (6.32)	28.48 (28.89)	13.98 (14.34)
2	$C_{12}H_{16}N_2S_4O_4Ni$	66	Light green	439	32.65 (32.8)	3.68 (3.64)	6.27 (6.3)	28.85 (29.15)	13.72 (13.36)
3	$C_{12}H_{16}N_2S_4O_4Se$	79	Light yellow	459	28.14 (27.98)	3.21 (3.35)	6.35 (6.28)	25.82 (26.25)	18.78 (18.98)

FTIR studies: The FTIR spectrum was recorded in the range of 4000-500 cm^{-1} using Perkin-Elmer FT-IR spectrophotometer. The absorption in region 1484-1410 cm^{-1} is due to C–N groups of the NCS_2 moiety, which has a partial double bond character. The frequencies detected in the region 965-946 cm^{-1} are attributed to the C–S vibrations show a bidentate bonding of the dithiocarbamate sulfur to the metal cation [19] (Fig. 1). The ν(CO) band in the free carboxylic acid group of amino acid occurs at 1715-1702 cm^{-1} in the spectra of the synthesized metal(II) complexes [4]. The metal-sulfur bonds are usually detected at the lower frequencey of 300 cm^{-1} [20,21]. The C-S stretching after the metal coordination has been shifted from 11 to 20 cm^{-1} lower range whereas the C-N stretching was shifted from 20 to 33 cm^{-1} higher range. It may be inferred from the data (Table-2) that coordination to metals occurs through the sulfur atoms of the ligand molecule, as the carboxylate anion is present in free amino acids but is changed to the carboxyl (-COOH) form in complexes [22].

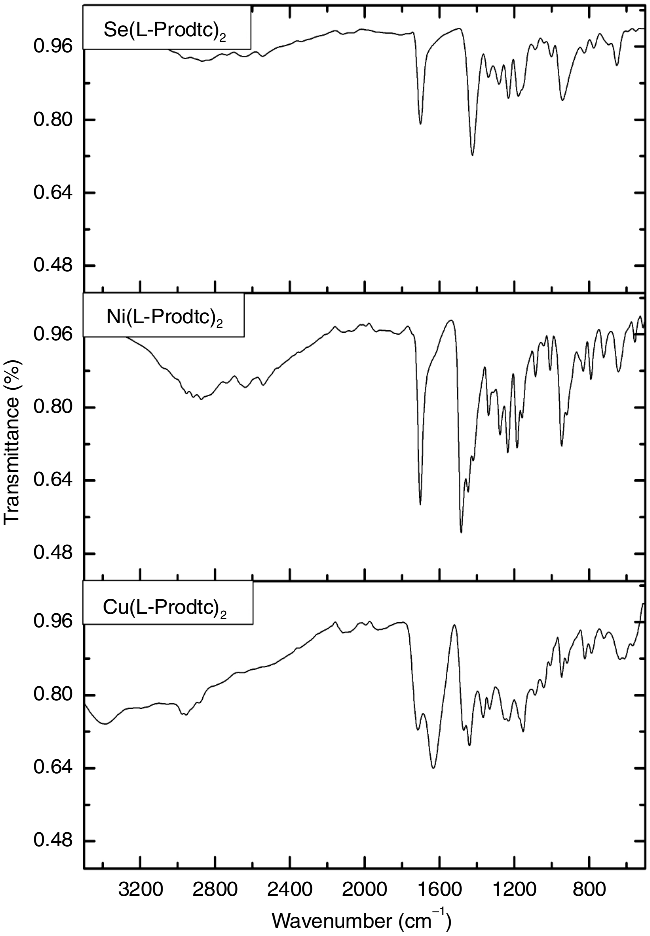


Fig. 1. IR spectra of Cu(L-Prodtc)$_2$, Ni(L-Prodtc)$_2$, Se(L-Prodtc)$_2$

TABLE-2
KEY IR FREQUENCIES (cm^{-1}) OF SYNTHESIZED COMPLEXES **1-3**

Observed frequencies	ν(CN)	ν_{as}(CS)	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$
Na_2(L-prodtc) ligand	1410	965	1610	1356
1	1470	946	1715	1336
2	1484	946	1703	1337
3	1424	943	1702	1339

Raman spectral studies: The Raman spectra indicate the presence of metal sulphur (M–S) coordination peaks below 500 cm^{-1} [23]. The CuS peak was appeared at 421 cm^{-1}, whereas the stretching bands corresponding to ν(Ni–S) and ν(Se–S) are obtained at 279 cm^{-1} and 400 cm^{-1}, respectively. In the Raman spectrum of synthesized M(L-Prodtc)$_2$ complexes, the absence of vibration frequencies for metal-oxygen (M-O) bands indicates that coordination occurs exclusively through the sulfur atoms [19,24].

UV-visible spectral studies: The UV-visible spectrum of synthesized M(L-Prodtc)$_2$ complexes in methanol was obtained between 200-800 nm. Fig. 2 shows the spectrum of absorption peaks of coordination compounds. The UV-visible spectrum of complexes **1** and **2** exhibit bands assigned to charge transfer (CT) of the L→M, the bands at λ_{max} 216 nm and 246 nm for the copper(II) and nickel(II) complexes. The bands at λ_{max} 269, 323 and 289 nm are due to the $\pi \rightarrow \pi^*$ intraligand transitions of the N–C–S group. A band at λ_{max} 296 nm arises from $\pi \rightarrow \pi^*$ transitions, but due to the S–C–S group and the bands at 432 and 400 nm are due to $d \rightarrow d$ transitions of complexes **1** and **2** peak at 389 nm attributes to MLCT of Ni(II) complex [25]. These results confirmed the formation of M(L-Prodtc)$_2$ and a tetrahedral geometry may be proposed for complexes **1-3** [21].

Magnetic property and molar conductance studies: The magnetic susceptibility measurements were also analyzed for the metal(II) complexes **1-3** using a VSM Lake Shore instrument. The magnetic susceptibility calculated values supported for M(L-Prodtc)$_2$ to be diamagnetic in nature [11-13]. The molar conductance of the M(L-Prodtc)$_2$ complexes was carried out in 10^{-3} M in methanolic solution for complex **1** and **3**, whereas DMSO was used for complex **2** [26]. The conductance value obtained in the range of 20.07-23.23 ohm^{-1} cm^2 mol^{-1} confirms that all the synthesized metal(II) complexes are neutral and covalent in nature.

NMR studies: The ^{1}H & ^{13}C NMR spectrum were recorded in DMSO and MeOD at room temperature using Bruker AVIII 500 MHz NMR spectrometer using TMS as reference. The ^{1}H NMR chemical shifts of M(L-Prodtc)$_2$ showed three multiplet resonance signals around δ 1.871-4.075 ppm is assigned to -CH_2 protons of 3CH_2, 2CH_2 and 4CH_2, respectively. The multiplet

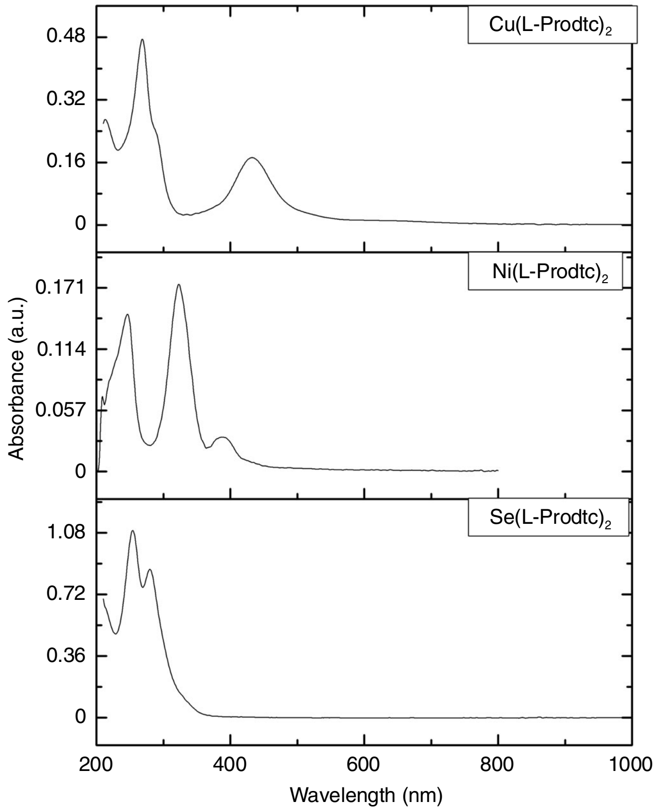


Fig. 2. UV-visible spectrum of Cu(L-Prodtc)$_2$, Ni(L-Prodtc)$_2$, Se(L-Prodtc)$_2$

resonance signals around δ 3.746-4.966 ppm are appropriate to -CH proton of located at 1CH position. The resonance around δ 4.804 ppm, δ 4.586 ppm and δ 5.389 ppm is due to 5COOH proton in complexes **1**, **2** and **3** [27]. In ^{13}C NMR, the C5 carboxylate carbon and C1-CH carbon of the ligand shows a singlet around δ (183.13, 174.45, 172.327) ppm and δ (59.47, 56.58, 68.260) ppm. The carbon of azolidine ring in ligand appears as a set of three reverberation signals [28,29]. The reverberation signals around 48.43 δ 28.55 and δ 23.49 ppm are of C3, C2 and C4 carbons of azolidine ring of L-Prodtc, respectively for complex **1**, δ (49.118 29.51, 22.646) ppm for complex **2** and is δ (51.818, 31.432, 28.812) ppm for complex **3** [30]. The resonance peak around δ (206.97, 204.97 and 192.812) ppm is assigned to the C6-CSS carbon [31-33].

Thermal studies: The metal(II) complexes were subjected to thermogravimetric analysis to study the thermal stability and their thermal behaviour in air atmosphere and in absence of air under non-isothermal conditions. The data are presented in Table-3 and depicted in Figs. 3-5, respectively. Thermogravimetric analysis data revealed that all the metal(II) complexes are stable up to 200 ºC except Se(L-Prodtc)$_2$, which is up to 160 ºC. The first step accompanied with the weight loss of one or two molecule of water or solvent molecule. The second stage between 205 and 350 ºC results in the synthesis of isothiocyanate, which is generated by the breakdown and rearrangement of L-Prodtc moiety into metal isothiocyanate [22], which also provides an evidence of metal coordination through sulphur atoms [31]. The third and fourth steps observed a constant weight loss of 32-43% between 300 and 900 ºC due to isothiocyanate breakdown into metal sulfide or sulphate, depending on the atmospheric conditions [34]. In fourth step, the breakdown is due the decomposition of metal sulfide and MSO_4 to form the corresponding metals in the range of 650-900 ºC. The slow step and the superposed step are the third and fourth steps of the disintegration process.

The TG-DTA process conducted in a nitrogen atmosphere yields metal sulphides as the resulting products for the comp-

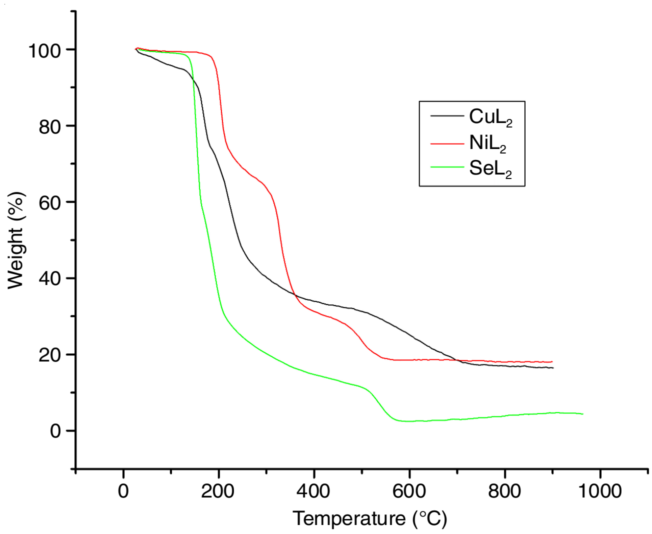


Fig. 3. TGA graph of Cu(L-Prodtc)$_2$, Ni(L-Prodtc)$_2$ and Se(L-Prodtc)$_2$

TABLE-3
THERMOGRAVIMETRIC ANALYSIS (TGA-DTG) DATA OF SYNTHESIZED COMPLEXES **1-3** OF L-PROLINE DITHIOCARBAMATE

Complexes	Decomposition range (°C)	Peak temperature (°C)	Weight loss (%)	Probable decomposition
Cu(L-Prodtc)$_2$	50-200	166.7	16.16	$CuL_22H_2O.EtOH \rightarrow CuL_2$
	200-300 (fast)	221.7	40.13	$CuL_2 \rightarrow Cu(SCN)_2$
	300-720 (slow	711.2	74.09	$Cu (SCN)_2 \rightarrow CuS$
	720-905 (fast)	902.2	83.50	$CuS \rightarrow Cu$
Ni(L-Prodtc)$_2$	100-250	204.5	14.94	$NiL_22H_2O.EtOH \rightarrow NiL_2$
	250-350 (fast)	329.0	49.41	$NiL_2 \rightarrow Ni(SCN)_2$
	350-650 (slow)	497.2	76.41	$Ni (SCN)_2 \rightarrow NiS$
	650-905 (fast)	900.4	81.91	$NiS \rightarrow Ni$
Se(L-Prodtc)$_2$	90-160 (fast)	155	20.51	$SeL_2 \rightarrow SeL$
	160-270 (fast)	198	61.3	$SeL \rightarrow Se$
	270-600 (slow)	545	94.35	Se→metal evaporates
		600	97.6	

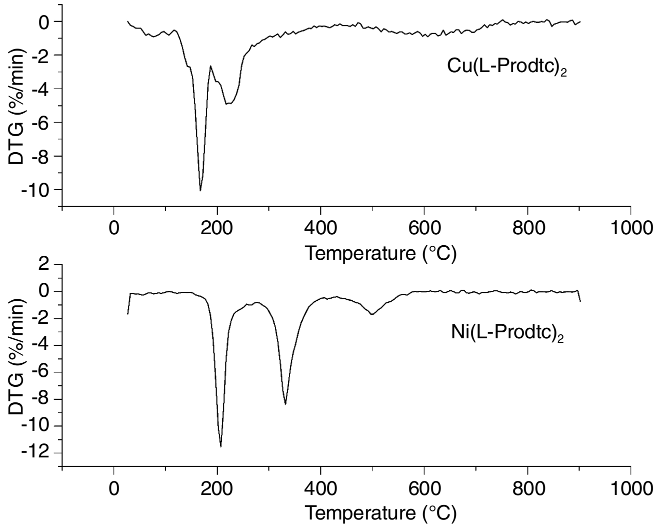


Fig. 4. DTG graph of Cu(L-Prodtc)$_2$ and Ni(L-Prodtc)$_2$

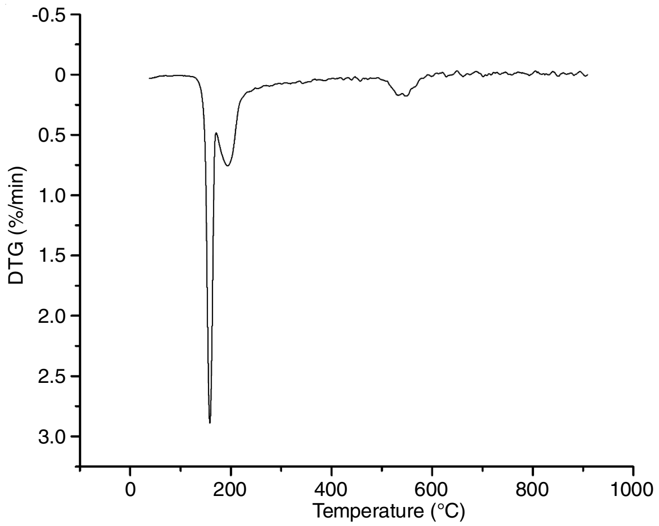


Fig. 5. DTG graph of Se(L-Prodtc)$_2$

lexes **1** and **2** [2,26,32,36-38]. In the TGA curve, a weight loss of 41.44%, which is equivalent to the molecular mass of 1 mole of ligand. In complex **3**, the second stage involves the rapid decomposition of the ligand that leaves behind the metal as residue at temperatures ranging from 160 ºC to 270 ºC. A weight loss of approximately 97.6% occurs during the third stage, which involves the gradual evaporation of the metal at approximately 600 ºC. This value suggests that both the selenium metal and the complex are volatile by nature [35].

Based on the aforementioned findings and considering the complex composition of dithiocarbamate, the following structure (Fig. 6) has been suggested for the metal(II) complexes of L-prolinedithiocarbamate.

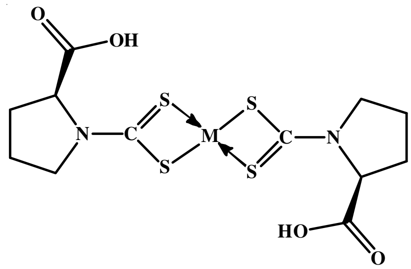


Fig. 6. Proposed structure of M(L-Prodtc)$_2$ (M = Cu, Ni, and Se)

Antibacterial studies: The antibacterial activitiy of all the three metal(II) complexes are presented in Table-4. Three bacteria *viz. Staphylococcus aureus*, *Pseudomonas aureginosa* and *Escherichia coli* were used in the screening. The synthesized metal(II) complexes showed the better inhibition activity against the bacteria. It was found that the sythesized complexes are active on *Staphylococcus aureus* in the order of copper(II) > nickel(II) > selenium(II) complexes. The inhibition ability of the metal(II) complexes were above 60% with comparison to the standard amphicillin [15,16].

Antifungal studies: The synthesized metal(II) complexes were tested against two fungi *viz. Trichoderma viridae* and *Candila albicans* using disc diffusion method. The results (Table-4) showed that metal(II) complexes had superior antifungal activity compared to L-Prodtc ligand [1]. Moreover, the metal(II) complexes show the moderate antifungal activity when compared to the standard amphotericin.

Anti-inflammatory studies: The synthesized metal(II) complexes were also studied for the anti-inflammatory activity. The absorbance against the blank was measured at 660 nm at room temperature and it has been observed that though all the metal(II) complexes exhibit the anti-inflammatory activities, copper(II) complex shows the remarkable percentage (81.44%) of activity [39], but slightly lower than the standard acetyl salicylic acid (Fig. 7).

Cytotoxicity nature: The synthesized dithiocarbamate metal(II) complexes were subjected to cytotoxicity analysis and found that the cell viability percentage of Cu(L-Prodtc)$_2$ is more than Ni^{2+} and Se^{2+} complexes (Fig. 8).

Antioxidant activity: All the three synthesized metal(II) complexes exhibited antioxidant activity beyond 50% with Se(II) complex demonstrating a remarkably high percentage of 87.2%, surpassing the standard BHT with 86.9%. Moreover, nickel(II) complex also displayed favourable findings of 81.19% [15] (Fig. 9).

TABLE-4
ANTIMICROBIAL ACTIVITY DATA OF LIGAND AND ITS L-Prodtc METAL(II) COMPLEXES

Compounds	Zone of inhibition (mm)				
	Antibacterial activity			Antifungal activity	
	Staphylococcus aureus	*Pseudomonas aeruginosa*	*Escherichia coli*	*Candida albicans*	*Trichoderma viridae*
L-Prodtc	8	6	8	8	8
Cu(L-Prodtc)$_2$	17	8	10	15	15
Ni(L-Prodtc)$_2$	15	6	8	15	15
Se(L-Prodtc)$_2$	16	8	9	13	14

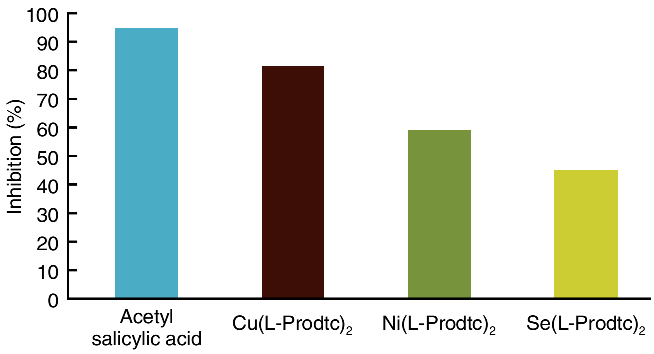


Fig. 7. Anti-inflammatory activity data of synthesized metal(II) complexes

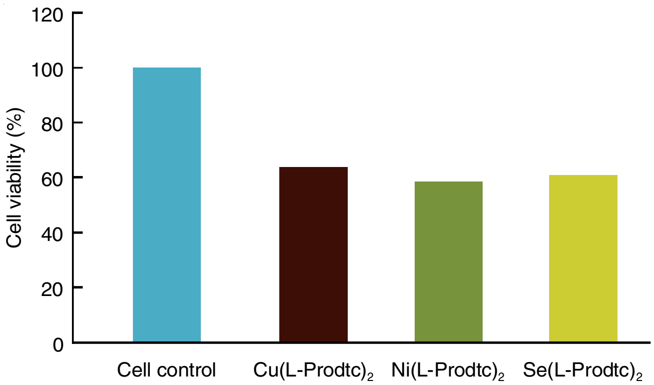


Fig. 8. Cytotoxicity activity of synthesized metal(II) complexes

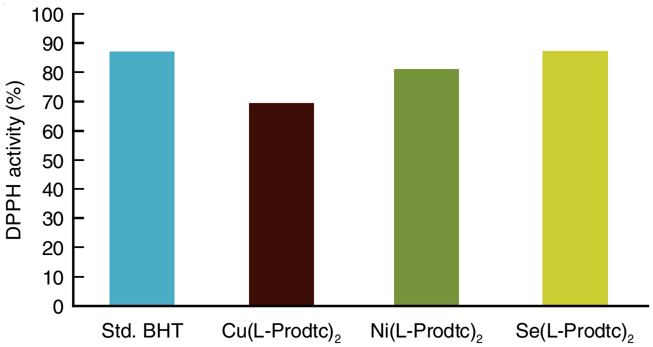


Fig. 9. Antioxidant activity of synthesized metal(II) complexes

Anticancer activity: Ligand L-Prodtc and Se(L-Prodtc)$_2$ were also analyzed for their anticancer activity. The Se(L-Prodtc)$_2$ was chosen because of the high biological importance and antioxidant property [40,41]. Both ligand and its Se(II) complex show a significant anticancer activity against the MCF-7 breast cancer cells. The MCF7 breast cancer cells exhibit a considerable decrease in cell viability at a dosage of 31.2 µg/mL, indicating that selenium(II) complex has a strong anticancer effect. The cell viability percentage is tabulated in Table-5.

TABLE-5
CELL VIABILITY (%) AND CONCENTRATION OF LIGAND AND SELENIUM(II)L-PROLINE DITHIOCARBAMATE COMPLEX

Compounds	MCF 7 breast cancer cells	
	Concentration (µg/mL)	Survivance (%) of cell
L-Prodtc	62.5	49.69
Se(L-Prodtc)$_2$	31.2	49.57

Conclusion

The ligand L-proline dithiocarbamate was synthesized in a single step, whereas its dithiocarbamate complexes (M = Ni^{2+}, Cu^{2+} and Se^{2+}) were also synthesized and characterized. The L-Prodtc ligand coordinated to the metal(II) ions can be assigned as uninegative and bidentate. The FT-IR data of the metal(II) complexes shows that only dithiocarbamate sulphur are coordinated to the metal(II) ions and not the carboxylate oxygens. The elemental analysis also confirmed the formation of L-Prodtc metal(II) complexes following 1:2 mole ratio as ML_2 type. The UV-visible spectra are very much similar to the anticipated values for the bivalent copper, nickel and selenium dithiocarbamate complexes. The observed changes in the L→M (LMCT) charge at λ_{max} 216, 246 and 289 nm indicate their relevance in the photochemical reactions. Based on the spectral data, the carboxylic acid (-COOH) group in L-Prodtc is not coordinated to the metal(II) cations. Among the synthesized metal(II) complexes,significant results have been observed from Se(II)L-Prodtc complex in antibacterial and biological activities, specifically in its anticancer action.The antioxidant activity of this complex is significantly higher than that of the standard BHT.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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