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Synthesis, characterization, thermal, antimicrobial and antioxidant studies of some transition metal dithiocarbamates

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Abstract Metal dithiocarbamate complexes of Co(II) [1], Cu(II) [2], Mn(II) [3], Cr(III) [4], and Pd(II) [5] have been synthesized using sodium *N*-ethyl-*N*-phenyldithiocarbamate (NaL). The complexes were characterized by elemental analyses, FTIR and UV–vis spectroscopic techniques, magnetic moment, molar conductance and thermal analyses (TGA and DSC). The infrared spectra indicated the coordination of dithiocarbamate through the two sulphur atoms in a symmetrical bidentate fashion. The thermal behavior of these complexes showed that the hydrated complexes lost water molecules in the first step, followed by decomposition of the ligand molecules in the final steps. Mass loss considerations at these final decomposition steps indicate conversion of the complexes to sulphides. The antimicrobial potentials of the complexes were evaluated against some selected bacteria strains (*Escherichia coli, Pseudomonas aureginosa, Salmonella typhi* and *Staphylococcus aureus*) and fungi organisms (*Aspergillus flavus* and *Fasiparium oxysporium*). The compounds showed a broad spectrum of fungicidal and bactericidal activities which exceeds that of the control drugs at a 100 μg/mL concentration. The antioxidant properties of the ligand and its Cu(II) complex were evaluated in vitro using DPPH assay, and the complex was found to exhibit better radical scavenging ability than the free ligand.

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Introduction

In the past two decades, the number of invasive and systemic pathogenic infections has increased dramatically [1] due to the growing number of immunocompromised patients as a result of cancer chemotherapy, organ transplantation and HIV infection [2, 3]. Consequently, drug resistance cases have become a growing concern in the treatment of infectious diseases caused by bacteria and fungi [4] organisms. For example, penicillin- and methicillin-resistant strains of *Staphylococcus aureus* (MRSA) are common in hospitals and are emerging in communities around the world [5]. Hence, the discovery and development of effective antibacterial and antifungal drugs with novel mechanisms of action have become urgent tasks for infectious disease research programs [6].

On the other hand, reactive oxygen species (ROS), such as the superoxide radical anion ($O_2^{-\cdot}$), hydroxyl radical ($OH^{\cdot}$) and hydrogen peroxide (H_2O_2) are formed in biological systems by the partial reduction of molecular oxygen [7]. Overproduction of ROS is considered to be the main cause of oxidative damage of biomolecules such as DNA, lipids and proteins, thereby accelerating cancer, ageing, inflammation, cardiovascular and neurodegenerative diseases [8]. Consequently, antioxidant-based research on synthetic and natural compounds has become one of the major areas of scientific research [9] that is channeled toward their ability to protect organisms and cells from damage induced by oxidative stress [10, 11]. The potential value of antioxidants has motivated scientists to search for the cooperative effects of compounds on improving antioxidant activity and cytotoxicity [12]. The DPPH (2,2′-diphenyl-1-picrylhydrazyl) assay is one of the most important and widely accepted methods used for the in vitro evaluation of antioxidant activity of both natural and synthetic compounds. It is technically a simple and rapid method for antioxidant screening [13]. DPPH radicals may be neutralized either by direct reduction via electron transfer or by radical quenching via proton transfer [14] and can be determined spectrophotometrically, or by high-performance liquid chromatography, or by using some faster and inexpensive methods like thin layer chromatography [13].

Most synthetic compounds have been reported to exhibit antioxidant properties [15, 16], however reports on the antioxidant potentials of dithiocarbamate compounds are scare, even though dithiocarbamate (DTC) moiety has been identified in a number of biologically active molecules [17, 18]. Our group has been interested in the biological properties of metal complexes of *N*-alkyl-*N*-phenyldithiocarbamates [17, 19, 20] and their usefulness as sources of metal sulfide deposition. Also, there have been numerous reports on the biological potentials of dithiocarbamate complexes [21–23]; hence, our interest in complexes of *N*-alkyl-*N*-phenyldithiocarbamates. Herein, we report the synthesis, spectroscopic, thermal and biological (antimicrobial and radical scavenging) studies of Co(II), Cu(II), Mn(II), Cr(III), and Pd(II) complexes of *N*-ethyl-*N*-phenyldithiocarbamate. The compounds were screened against Gram-negative strains (*Escherichia coli and Salmonella typhi*) and Gram-positive bacteria strains (*Pseudomonas aureginosa* and *S. aureus*) and fungi organisms (*Aspergillus flavus* and *Fasiparium oxysporium*). The microbial strains were chosen based on their clinical and pharmacological importance [24]. In addition, thermal studies of the compounds were conducted in order to investigate the potentials of the complexes as single-source precursors in metal sulphide depositions [25].

Experimental

General

All reagents and solvents were commercially available high-grade materials (Merck/Sigma-Aldrich) and were used as received. The solvents were purified by standard methods [26].

Physical measurements

Elemental analysis was performed on an Elementar vario EL Cube set up for carbon, hydrogen, nitrogen and sulfur (CHNS) analysis. Infrared (IR) spectra were recorded on a Bruker alpha-P Fourier transform IR (FTIR) spectrometer in the frequency range 4000–500 cm^{-1}. The electronic spectra of the metal complexes were recorded on a Perkin-Elmer λ20 ultraviolet–visible light (UV–Vis) spectrophotometer in chloroform. Room-temperature magnetic moments and molar conductance measurements were recorded on a Johnson Matthey magnetic susceptibility balance and a MC-1 Mark V conductivity meter with a cell constant of 1.0, respectively. The thermal behaviour of the complexes was studied using the simultaneous thermal analysis (STA) technique for parallel recording of TG (thermogravimetry) and differential scanning calorimetry (DSC) curves on an SDTQ 600 Thermal instrument. Samples were contained within alumina crucibles and heated at 10 °C/min (under nitrogen), from room temperature to 800 °C.

Preparation of the ligand sodium *N*-ethyl-*N*-Phenyldithiocarbamate, NaL

Carbon disulphide (6.0 mL, 0.1 mol) was added in small portions to an equimolar mixture of sodium hydroxide dissolved in minimum quantity of water (4.0 g, 0.1 mol) and *N*-ethyl aniline (12.8 mL, 0.1 mol), and cooled in an ice bath at 0 °C. After stirring for 3 h, the solidified mass was isolated from the solution and recrystallized in acetone. The product was collected, rinsed with diethyl ether and dried under vacuum over $CaCl_2$ at room temperature [27].

Preparation of the complexes ML_2 (M=Co, Cu, Mn) and CrL_3

Ethanol solution (20 mL) of the respective hydrated metal nitrate ($Co(NO_3)_2·6H_2O$: 0.87 g, 0.003 mol; $Cu(NO_3)_2·3H_2O$: 0.72 g, 0.003 mol; $Mn(NO_3)_2·4H_2O$: 0.75 g, 0.003 mol; $Cr(NO_3)_3·9H_2O$: 0.80 g, 0.002 mol) was added with stirring to 25 mL of ethanol solution of sodium *N*-ethyl-*N*-phenyldithiocarbamate (1.31 g, 0.006 mol). The reaction mixture was stirred for 1 h, and the colored, precipitated complexes were filtered off, washed with water, then cold ethanol, followed by diethyl ether and dried in vacuum.

$[CoL_2]$ (**1**), yield: 1.10 g, 81 %. Selected IR, ν(cm^{-1}): 1465 (C=N), 1278 (C_2–N), 912 (C=S). Anal. Calc. for $C_{18}H_{20}N_2S_4Co$ (451.56): C, 47.88; H, 4.46; N, 6.20; S, 28.40. Found: C, 47.22; H, 4.32; N, 6.10; S, 28.07 %. Electronic spectra (cm^{-1}): 25,560, 37,857, 19,231, and 22,293 ($\varepsilon = 260$ ı mol^{-1} cm^{-1}); Conductance (Ω^{-1} cm^2 mol^{-1}):32.62; μ_{eff} (B.M): 4.38.

$[CuL_2]$ (**2**), yield: 1.21 g, 88 %. Selected IR, ν(cm^{-1}): 1490 (C=N), 1282 (C_2–N), 908 (C=S). Anal. Calc. for $C_{18}H_{20}N_2S_4Cu$ (456.17): C, 47.39; H, 4.42; N, 6.14; S, 28.12. Found: C, 47.18; H, 4.42; N, 6.21; S, 28.47 %. Electronic spectra (cm^{-1}): 26,750, 37,870, 19,567, and 22,390 ($\varepsilon = 203$ ı mol^{-1} cm^{-1}); Conductance (Ω^{-1} cm^2 mol^{-1}):18.32; μ_{eff} (B.M): 1.95.

$[MnL_2]·0.25H_2O$ (**3**), yield: 0.94, 70 %. Selected IR, ν(cm^{-1}): 1460 (C=N), 1268 (C_2–N), 920 (C=S). Anal. Calc. for $C_{18}H_{21}N_2S_4O_{0.25}Mn$ (452.07): C, 47.82; H, 4.57; N, 6.19; S, 28.37. Found: C, 48.22; H, 4.52; N, 6.20; S, 28.67 %. Electronic spectra (cm^{-1}): 25,340, 37,852, 09,231, and 12,293 ($\varepsilon = 324$ ı mol^{-1} cm^{-1}); Conductance (Ω^{-1} cm^2 mol^{-1}):48.09; μ_{eff} (B.M): 5.72.

$[CrL_3]·2H_2O$ (**4**), yield: 0.88 g, 69 %. Selected IR, ν(cm^{-1}): 1472 (C=N), 1228 (C_2–N), 912 (C=S). Anal. Calc. for $C_{27}H_{34}N_3S_6O_2Cr$ (676.96): C, 47.90; H, 5.06; N, 6.21; S, 28.42. Found: C, 48.02; H, 4.75; N, 6.43; S, 28.87 %. Electronic spectra (cm^{-1}): 25,176, 37,849, 23,729, and 17,280 ($\varepsilon = 65$ ı mol^{-1} cm^{-1}); Conductance (Ω^{-1} cm^2 mol^{-1}):26.32; μ_{eff} (B.M): 3.20.

Preparation of $[PdL_2]·4H_2O$ (5)

Sodium *N*-ethyl-*N*-phenyldithiocarbamate (1.10 g, 0.005 mol) dissolved in 25 mL of distilled water was added dropwise to 25 mL of cold aqueous solution of palladium chloride (0.45 g, 0.0025 mol) in an ice bath at 0 °C. The reaction mixture was stirred for 12 h, and the solids were filtered by suction, washed with water, ethanol and diethyl ether, and dried invacuo. Yield: 0.92, 61 %. Selected IR, ν(cm^{-1}): 1497 (C=N), 1308 (C_2–N), 920 (C=S). Anal. Calc. for $C_{18}H_{28}N_2S_4O_4Pd$ (571.10): C, 37.85; H, 4.94; N, 4.91; S, 22.46. Found: C, 37.170; H, 4.62; N, 5.01; S, 22.37 %. Electronic spectra (cm^{-1}): 27,490, 38,650, 19,74, 22,398 ($\varepsilon = 310$ ı mol^{-1} cm^{-1}); Conductance (Ω^{-1} cm^2 mol^{-1}): 28.07; μ_{eff} (B.M): 0.34.

Antimicrobial studies

Antibacterial and antifungal screenings were conducted using a disc diffusion method [28]. Petri plates were prepared with 20 mL of sterile Mueller–Hinton agar

(MHA). The test cultures were swabbed on the top of the solidified media and allowed to dry for 15 min. A specific amount (25 µL from the 100 µg/mL) of the compound was introduced into each disc. The loaded discs were placed on the surface of the medium and left for 30 min at room temperature for compound diffusion. The negative control was dimethyl sulfoxide (DMSO). The plates were incubated for 24 h at 37 °C for the bacteria and 48 h at 30 °C for the fungi strains. Zones of inhibition were recorded in millimeters and the experiments were repeated twice. The bacteria strains were *E. coli, P. aureginosa, S. typhi and S. aureus, w*hile the fungi organisms were *A. flavus* and *F. oxysporium*. Streptomycin and ketoconazole were used as the positive control drugs.

Minimum inhibitory concentration (MIC)

MIC studies of the complexes were carried out following a standard method for bacteria and fungi [20]. Different concentrations (50, 40, 30, 25, 15, 10 µg/mL) of the compounds were dissolved in DMSO (2 %). The solutions were added to each medium in 96-well plates. An inoculum of 100 µL from each well was inoculated. Ketoconazole (as an antifungal agent) and streptomycin (as antibacterial agent) were included in the assays as positive controls. The plates for the fungi were incubated for 48–72 h at 30 °C and 24 h at 37 °C for the bacteria. The MIC for the fungi is the lowest sample concentration, showing no visible fungal growth after incubation time. About 5 µL of the tested broth was placed on the sterile MHA plates for bacteria and incubated at respective temperature. The MIC for bacteria was determined as the lowest concentration of the compound inhibiting the visual growth of the test cultures on the agar plate.

Antioxidant studies

To evaluate the antioxidant activity, stock solution (1 mg/mL) of the samples was diluted to 100–500 µg/mL. Ethanol solution of DPPH (1 mL, 0.3 mmol) was added to DMSO (2 mL) solutions of the sample at different concentrations [29]. The mixture was shaken vigorously and allowed to stand at room temperature for 30 min. The absorbance was then measured at 517 nm using a UV–Vis spectrophotometer. The lower absorbance of the reaction mixture indicates higher free radical scavenging activity. Ethanol was used as the solvent and ascorbic acid as the standard. The DPPH radical scavenger was calculated using the Eq. (1):

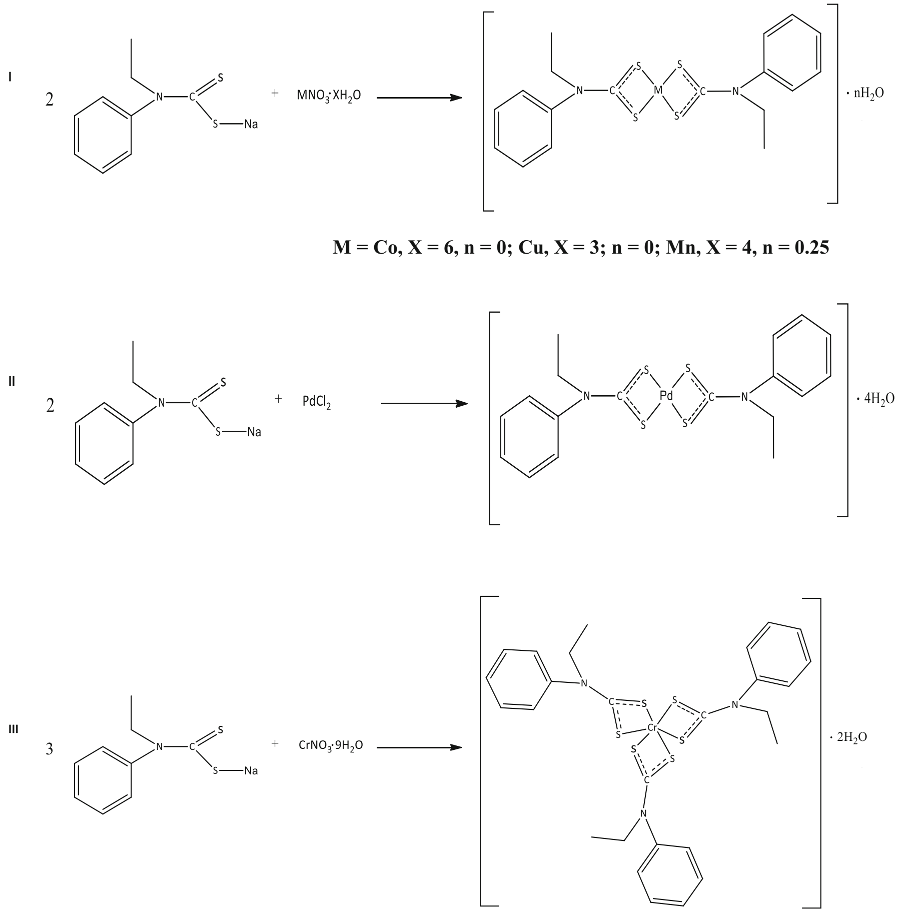
$$\text{DPPH Radical Scavenging Effect } (\%) = A_o - \frac{A_1}{A_0} \times 100 \tag{1}$$

A_0 is the absorbance of the control reaction and A_1 is the absorbance in the presence of the samples or standards.

Results and discussion

Syntheses

The reaction between the ligand, sodium *N*-ethyl-*N*-phenyldithiocarbamate (NaL) and Co(II), Cu(II), Mn(II), Cr(III) and Pd(II) salts resulted into the respective metal dithiocarbamate complexes through a displacement reaction as shown in Scheme 1. The coordination of the ligand to the respective metal ion in the complexes is by a bidentate fashion through two sulphur atoms in a 2:1 stoichiometry for complexes **(1), (2)**, **(3)** and **(5),** but in a 3:1 stoichiometric reaction for complex **(4)**. The metal complexes are soluble in chloroform, dicholoromethane, acetone and coordinating solvents like dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The analytical data are in good agreement with the proposed structure of the complexes. Results of spectral and thermal studies of the complexes are consistent with their



M = Co, X = 6, n = 0; Cu, X = 3; n = 0; Mn, X = 4, n = 0.25

Scheme 1 Synthesis pathway for (**I**) Co, Cu, and Mn; (**II**) Pd and (**III**) Cr complexes formulation, and are in concordance with other similar dithiocarbamate complexes [17–23].

FTIR spectral studies

The IR spectra of the complexes were compared with those of free ligand [27, 30] in order to determine the coordination sites that may be involved in the complex formation. All the complexes showed C–N stretching vibration of the dithiocarbamate moiety in the region of 1460–1497 cm^{-1}. The position of this band is indicative of the degree of the partial double-bond character in the C–N bond (ν(C=N) = 1640–1690; ν(C–N) = 1250–1360 cm^{-1}) [31–33]. In the spectrum of the ligand, the C–N band was observed at 1453 cm^{-1} [27]. The appearance of this band at a lower frequency in the free ligand compared to the metal complexes is ascribed to the delocalization of electron toward the metal centre upon coordination to the metal atoms [32–35]. The spectra of the Mn, Cr and Pd complexes (**3, 4** and **5**) showed broad bands around 3430 cm^{-1} and sharp peaks around 1605 cm^{-1} which could be ascribed to ν(O–H) stretching and δ(O–H) bending vibrations, respectively. On the other hand, a decrease in the ν(C–S) stretching band is observed relative to the free ligand. The ν(C=S) band is observed as an isolated band in the 908–920 cm^{-1} range in all the complexes and is indicative of a bidentate dithiocarbamate [36].

Magnetic measurements and molar conductivity measurements

The magnetic susceptibility of all the synthesized complexes was measured in a solid state at room temperature. The occurrence of high spin (d^7) cobalt (II) was confirmed by the observed magnetic moment value of 4.38 BM for **(1)**. The magnetic moment of high spin cobalt compounds in a cubic environment ranges from 4.20–5.20 B.M and high spin octahedral Co (II) complexes are between 4.70 and 5.20 B.M, while tetrahedral Co(II) complexes have moments in the range 4.20–4.60 B.M [37]. Therefore, complex **(1)** was assigned a tetrahedral geometry. A high spin d^9 copper center was confirmed for complex **(2)** with a magnetic moment of 1.95 B.M. Mononuclear Cu(II) complexes have magnetic moments in the range 1.9–22 B.M [38], which is usually higher than the spin-only value of 1.73 B.M due to orbital contribution and spin–orbit coupling [39]. Hence, complex **(2)** is a mononuclear four-coordinate complex. Chromium in a +3 oxidation state is a d^3 system. The Cr(III) complex, **(4),** has a magnetic moment of 3.2 B.M, which supports the high spin octahedral geometry [34]. The Pd complex, **(5),** showed a magnetic moment value of 0.34 B.M which is expected for a square planar geometry for the palladium (II) complex due to diamagnetism [40]. The effective magnetic moments of a high spin mononuclear Mn(II) complexes are expected to be close to the spin-only value of 5.90 B.M. Since the ground term is $^6A_1$, there is no orbital contribution [41]. A magnetic moment value of 5.72 B.M. was observed for complex **(3).**

The metal complexes were dissolved in DMSO and the molar conductivities of 10^{-3} -M solution at room temperature were measured [42]. The low molar conductance values (18.32–48.09 Ω^{-1} cm^2 mol^{-1}) of the complexes support their non-electrolytic nature [43].

Electronic spectra

The electronic absorption bands of the complexes are classified into two distinct groups. Transitions due to the ligand appeared in the UV region while d–d transitions appeared in the visible region. These transitions were assigned with respect to the structures of the complexes. The UV–visible spectra of the complexes were recorded in DMSO and two bands were exhibited in the UV region around 25,340–27,490 cm^{-1} and 37,849–38,650 cm^{-1} due to n–π* and π–π* transitions, respectively, from the dithiocarbamate ligand [19]. Additional bands around 23,729 ($\varepsilon = 80$) and 17,280 cm^{-1} ($\varepsilon = 65$) were observed in the visible region of the spectra for the Cr(III) complex (**4**), which were assigned to $^4A_2g(F) \rightarrow {}^4T_1g(F)$, $^4A_2g(F) \rightarrow {}^4T_1g(P)$ transitions, respectively. This was in agreement with other reported similar octahedral Cr(III) complexes [44]. Octahedral d^9 copper complexes are expected to have a broad bands due to $^2Eg \rightarrow {}^2T_1g$ with a ^2D ground term due to Jahn–Teller distortion. However, a Jahn–Teller effect caused by asymmetrical filling of the, e_g set of orbitals, causes a splitting of ^2Eg and ^2T_2g into ^2B_1g, ^2A_2g and ^2B_2g, ^2Eg, respectively, which is usually observed [45]. Hence, the transitions may lie within one envelope or may resolve into two or three absorption band components. For tetrahedral d^9 copper complexes, the effects of a Jahn–Teller effect is less pronounced as it is the T_2 set of orbitals that are asymmetrically filled. A broad band below 10,000 cm^{-1} is usually observed in this case. Square planar d^9 copper complexes usually show two bands of high energy above 10,000 cm^{-1}. Therefore, the non-appearance of bands below 10000 cm^{-1} in the copper complex indicates the absence of a tetrahedral geometry [38, 44]. The copper complex showed absorption bands in the visible region at 19,567 cm^{-1} ($\varepsilon = 102$) and 22,390 cm^{-1} ($\varepsilon = 108$) due to $^2B_2g \rightarrow {}^2B_1g$ and $^2B_2g \rightarrow {}^2A_2g$ transitions of a square planar geometry. This observation is similar to other reported copper (II) complexes of square planar geometry [17]. The Co(II) complex (**1**) displayed two bands, one at 15,806 cm^{-1} ($\varepsilon = 122$) and one at 19,698 cm^{-1} ($\varepsilon = 156$) which were assigned to $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$ transitions, respectively, of a tetrahedral geometry [43, 44, 46, 47]. This supports the proposed geometry inferred from the magnetic moment. The spectrum of the Pd(II) complex (**5**) showed two absorption bands at 19,231 ($\varepsilon = 118$) and 22,293 cm^{-1} ($\varepsilon = 125$), typical of square planar geometry, which are assigned to $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1E_2g$ transitions [48]. The spectrum of the Mn(II) complex (**3**) showed two absorption bands at 11,985 cm^{-1} ($\varepsilon = 0.238$) and 12,293 cm^{-1} ($\varepsilon = 347$), typical of tetrahedral geometry, which were assigned to $^6A_1g \rightarrow {}^4E_1g$ and $^6A_1g \rightarrow {}^4A_1g$ transitions [49, 50].

Thermal decomposition of the complexes

The temperature range of the main decomposition stage, peak temperatures, and weight of final residues, observed in each step of TG/DTG/DSC curves for

Table 1 Thermal analysis data of complexes

Compounds	$[CoL_2]$	$[CuL_2]$	$[CrL_3]\cdot 2H_2O$	$[PdL_2]\cdot 4H_2O$	$[MnL_2]\cdot 0.25H_2O$
Temp. range of main decomp. (°C)	261–375	197–360	241–414	211–395	230–351
DTG peak T (°C)	350	301	347	262	292
Melting point	205	176	256	198	192
DSC peak, T (°C)	350	303	351	264	294
Mass of residue (mg)					
Found	1.16	2.45	3.87	3.85	2.67
Calc.	1.12	2.66	3.40	3.58	2.49

complexes **1**–**5** are given in Table 1. In all the complexes, there was no formation of a thiocyanate intermediate. Metallic thiocyanates are common intermediates in the thermal decomposition of dithiocarbamate complexes [51–53].

Thermal decomposition of $[CoL_2]$ (1)

According to the TG and DSC curves (Fig. 1), complex (**1**) undergoes three endothermic processes. The first stage, which occurred in the 145–165 °C temperature range, is not associated with any weight loss and could be attributed to a crystalline phase change [54], followed by a melting process at 205 °C. The proposed anhydrous formulation from the elemental analysis result is supported by lack of any mass loss up to 275 °C, indicating the absence of lattice or coordination water molecules [55]. Finally, the third stage of decomposition which occurred

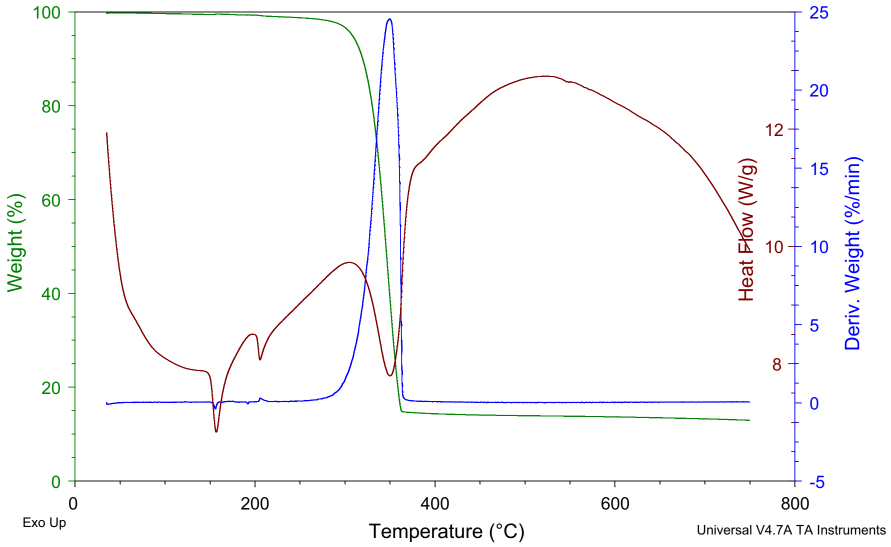


Fig. 1 TG/DTG and DSC curves of the compounds $[\mathbf{CoL_2}]$ **(1)** obtained in nitrogen atmosphere (75 mL/min), heating rate 10 °C/min

between 261 and 375 °C is associated with the breakdown of the dithiocarbamate ligand molecule and subsequent formation of CoS (found/calcd. mass of residue: 1.16/1.12 mg).

Thermal decomposition of [CuL_2] (2)

The thermal decomposition of complex (**2**) involves two endothermic peaks (Fig. 2). The first endothermic peak at 176 °C is the melting temperature. After melting, the complex undergoes a fast mass loss of the most of the organic ligand in the temperature range 197–360 °C, and this was accompanied by an endothermic effect with peak temperature at 303 °C. According to the DTG curve, the maximum rate of decomposition occurred at 301 °C and the resultant residue confirmed CuS (found/calcd. mass of residue: 2.45/2.66 mg). In similar studies involving the thermal behavior of copper (II) dithiocarbamates in nitrogen and air environments, mass loss considerations at the main decomposition stages in N_2 environments indicated conversion of the complex to sulphides [56]. However, under the air changes which corresponded to the formation of sulphide, oxidation of sulphide to sulphate and the decomposition of sulphate to oxide were suggested [57]. The thermal decomposition of copper bis(diethyldithiocarbamate) yielded cuprous sulphide (Cu_2S) nanocrystals [58].

Thermal decomposition of [MnL_2]·0.25H_2O (3)

The decomposition pattern of the complex showed a weak endothermic peak at 135 °C, which is ascribed to the loss of lattice water. This stage was followed by an endothermic decomposition stage which occurred without any observed weight loss

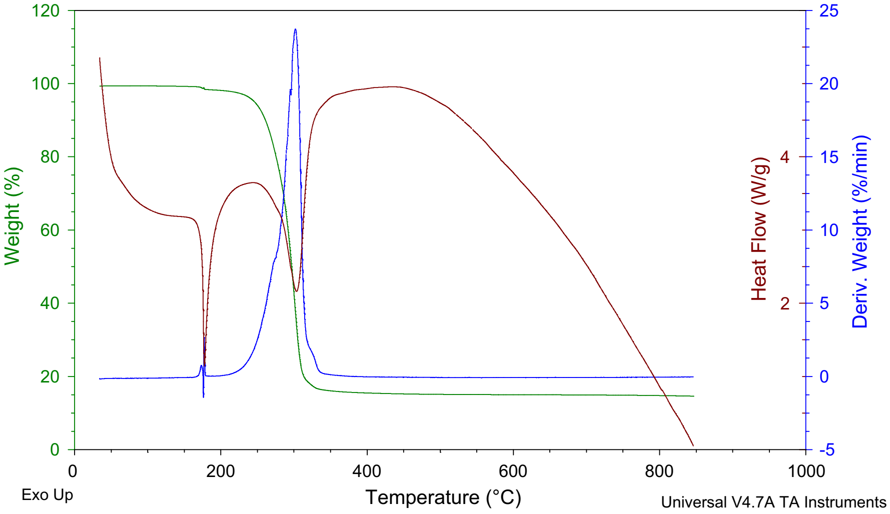


Fig. 2 TG/DTG and DSC curves of the compounds [**CuL_2**] **(2)** obtained in nitrogen atmosphere (75 mL/min), heating rate 10 °C/min

in the TG (Fig. 3). This is ascribed to the melting of the complex, and it is followed by a huge weight loss in the temperature range 230–351 °C accompanied by a strong endothermic effect in the DSC curve. The temperature of maximum rate of decomposition for this stage is 292 °C. At the end of the decomposition, residues of manganese sulphide were left (found/calcd. mass of residue: 2.67/2.42 mg). The decomposition of Mn(II) complex of cyclic dithiocarbamates under air presented a mass gain, probably due to the oxidation of the metal centre and Mn_2O_3 and $MnSO_4$ as decomposition products. However, MnS was obtained under a nitrogen atmosphere [59]. Similarly, MnO and MnS have been obtained as the final residue of the thermal decomposition of manganese (II) diethyldithiocarbamate studied in air and nitrogen environments, respectively [60].

Thermal decomposition of $[CrL_3]\cdot 2H_2O$ (4)

Thermal analysis showed that the first thermal effect on the decomposition of the Cr(III) complex began at slightly above room temperature (Fig. 4) and continued up to 105 °C. A weight loss corresponding to the removal of two molecules of water of crystallization (DTG maximum at 80 °C) was observed with an endothermic peak at 84 °C. The anhydrous compound then melted around 256 °C, and afterwards the liquid compound decomposed in a single well-defined step from 241 to 414 °C, comprising the breakdown of the organic ligand and the formation of Cr_2S_3 (found/calcd. mass of residue: 3.87/3.40 mg). The thermal decomposition of a series of Cr(III) dithiocarbamates studied in the 20–600 °C temperature range showed that the final product of the decomposition was chromium sulphide Cr_2S_3 or with

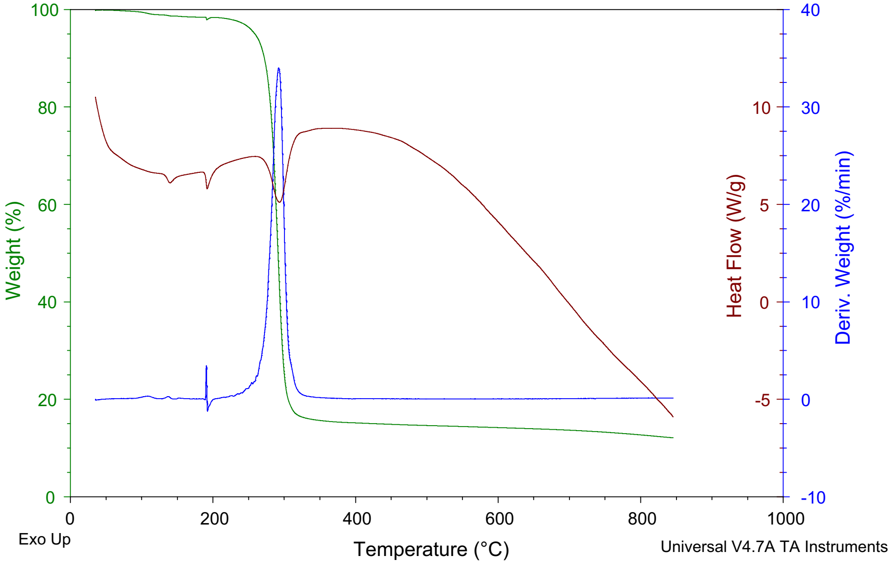


Fig. 3 TG/DTG and DSC curves of the compounds $[MnL_2]\cdot 0.25H_2O$ (**3**) obtained in nitrogen atmosphere (75 mL/min), heating rate 10 °C/min

incompletely combusted sulphur atoms [61]. In similar studies [62], the residue was a mixture of Cr_2S_3 and deficient sulphur chromium sulphides.

Thermal decomposition of $[PdL_2]\cdot 4H_2O$ (5)

The thermal behavior of complex (**5**) is in accordance with the proposed hydrated formulation (Fig. 5). The presence of lattice (crystallisation) water could be correlated to the first mass loss which began around 90 °C with a peak at 136 °C. About 13 % mass loss occurred which corresponds to 4 molecules of water. Thus, the first endothermic mass loss corresponds to the release of lattice water molecules and the second endothermic peak at 198 °C (which occurred without any noticeable weight loss) is ascribed to the melting temperature of the complex. In the following step (211–395 °C), decomposition of the ligand molecule occurred. The thermal decomposition ends at about 410 °C leaving as residue PdS_2 (found/calcd. overall mass loss: 3.85/3.58 mg). Thermal studies of palladium (II) complexes with dithiocarbamate derivatives carried out in synthetic air showed the formation of PdS as an intermediate product which further undergoes sulphur oxidation leading to the partial oxidation of the PdS to PdO. Upon further heating, the compound decomposed to metallic palladium [63]. TG analysis of a series of pyridine solvated and non-solvated palladium dithiocarbamate complexes studied under nitrogen atmosphere showed decomposition steps which leaves a residue of PdS [64]. Palladium sulphide has been reported to exist in different phases such as PdS, PdS_2, $Pd_{2.8}S$, Pd3S, Pd_4S, $Pd_{2.2}S$ and $Pd_{2.5}S$. Thus, the product of thermal

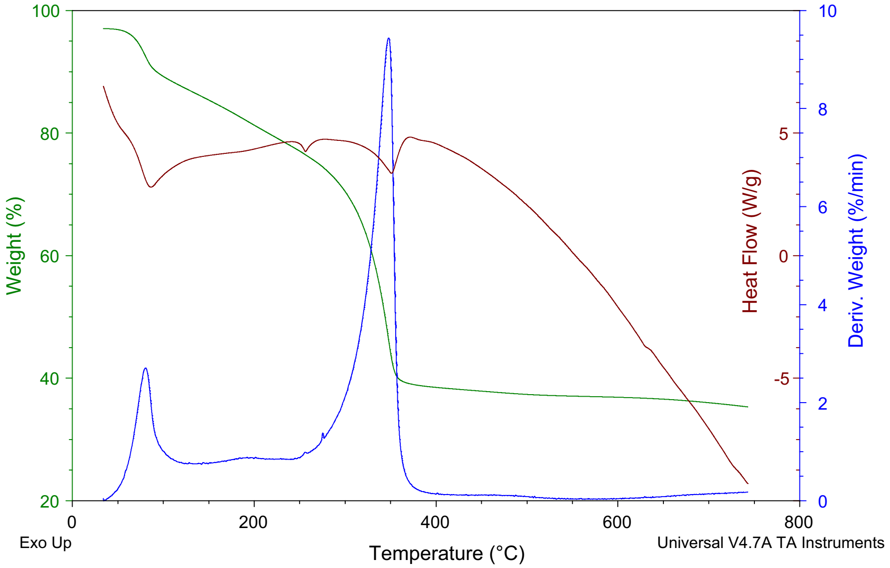


Fig. 4 TG/DTG and DSC curves of the compounds $[CrL_3]\cdot 2H_2O$ (**4**) obtained in nitrogen atmosphere (75 mL/min), heating rate 10 °C/min

decomposition of complexes is influenced by the metal, the substituent on the ligand, the heating rate and also the thermal environment [65].

Antimicrobial studies

The basic principle in the design of any active antimicrobial compound is to inhibit the growth of pathogens without any side effects on treatment. Antimicrobial activity of the ligands, metal complexes, and standard drugs were screened against Gram-positive and Gram-negative bacterial strains to evaluate their potentials as antibiotics. The antimicrobial analysis of the complexes was conducted and the results are presented in Table 2 and Fig. 6. The complexes showed moderate to good antimicrobial activity at a concentration of 100 µg/mL against the bacteria strains (*E. coli, P. aureginosa, S. typhi* and *S. aureus*) and fungi organisms (*A. flavus* and *F. oxysporium*). Complex **2** displayed the best activity against *S. aureus* compared to other complexes and streptomycin. Similarly, the activities of (**1**) and (**4**) exceeded streptomycin against *S. aureus*. Complex (**4**) showed the best activity against *P. aureginosa* compared to the other complexes and the control drug. Complex (**3**) had the best activity against *S. typhi* and *E. coli* compared to the other complexes and the control drug. In general, the complexes displayed better activity as antibacterial agents than as antifungal agents when compared to streptomycin and ketoconazole. However, complex (**5**) did not show any antimicrobial activity and, hence, was excluded from Table 2. This might be as a result of its bulkiness which results in reduction in the cell membrane permeability of the complex. The antimicrobial results of the complexes are comparable to similar works reported in

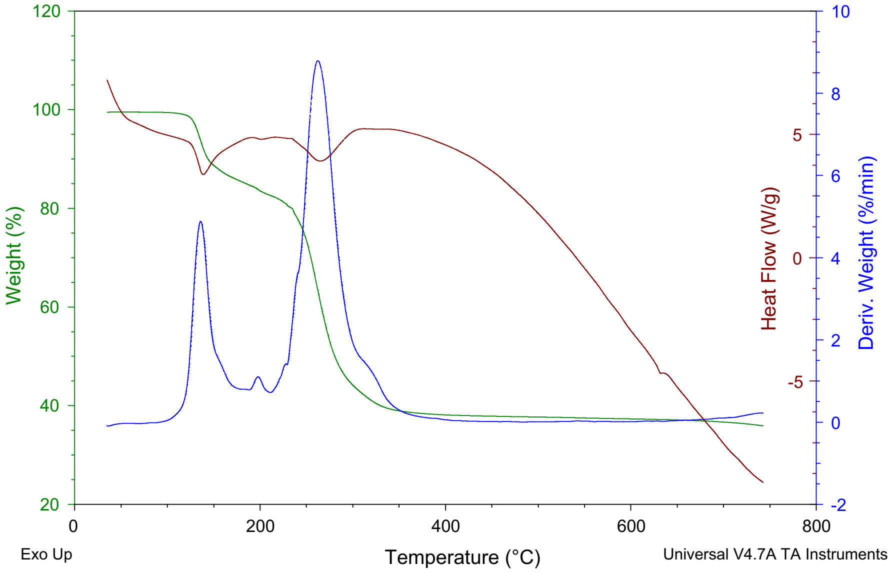


Fig. 5 TG/DTG and DSC curves of the compounds $[PdL_2]\cdot 4H_2O$ (**5**) obtained in nitrogen atmosphere (75 mL/min), heating rate 10 °C/min

Table 2 Antimicrobial data for the complexes and control drugs

Name	*Aspergillus flavus*	*Fasiparium oxysporium*	*Staphylococcus aureus*	*Pseudomonas aureginosa*	*Escherichia coli*	*Salmonella typhi*
NaL	09	10	0	10	04	07
[CoL$_2$]	R	R	24	15	R	18
[CuL$_2$]	10	12	27	18	10	13
[MnL$_2$]·0.25H$_2$O	14	R	R	R	25	16
[CrL$_3$]·2H$_2$O	18	16	26	27	R	R
Streptomycin	–	–	22	24	20	23
Ketoconazole	20	22	–	–	–	–

Values (in mm) represent the mean of two replications; streptomycin standard antibacterial agent, ketoconazole standard antifungal agent, 'R' resistant, "–" not screened

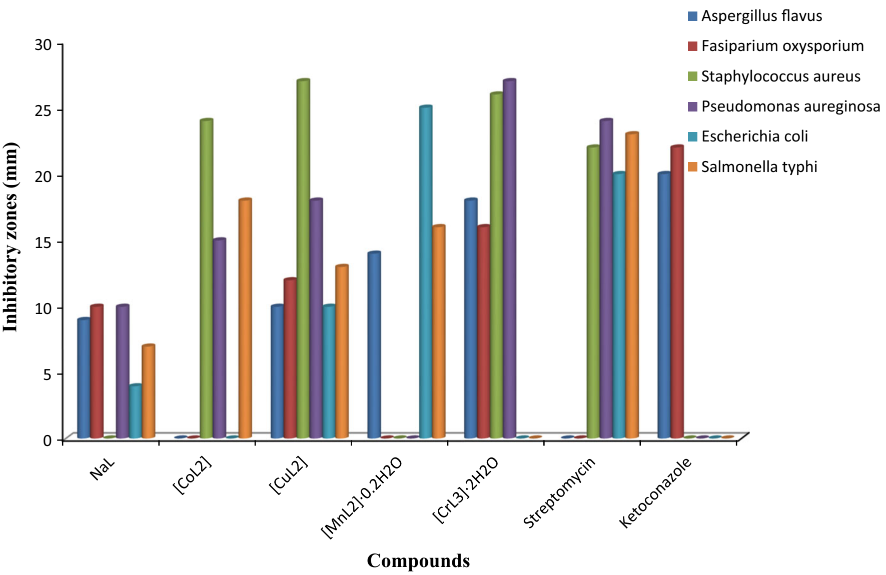


Fig. 6 Histogram representing antimicrobial data for the complexes

literature for dithiocarbamate compounds [17]. Overall, the complexes showed better antimicrobial activity than the free ligand due to chelation (Fig. 7).

The minimum inhibitory concentrations of the complexes were conducted at different concentrations (50, 40, 30, 25, 15, 10 µg/mL,) and are presented in Table 3. From the data, complexes with good antimicrobial activity also showed low MIC which reflects their potentials as microbial inhibitors.

Antioxidant studies

DPPH Radical scavenging ability

2,2-Diphenyl-1-picrylhydrazyl (DPPH) is a stable organic radical compound and its oxidative assay is used extensively in the quantification of the radical-scavenger capacity or hydrogen-donor ability of samples. Antioxidants that exhibit DPPH scavenging activity are continuously receiving attention. Compounds with antioxidant properties could be expected to offer protection in rheumatoid arthritis and inflammation and to lead to potentially effective drugs [66, 67]. DPPH is a stable free radical, which can accept an electron or proton radical and, in turn, gets converted into a stable diamagnetic molecule. DPPH has a strong absorption band at 517 nm due to the presence of an odd electron in the molecule [68]. In the present study, the ability of the ligand NaL and Cu(II) complexes to act as proton radical (Na^+) donors for the transformation of DPPH into its reduced form was investigated. The absorbance decreases due to change of color from purple to yellow as the radical is scavenged by the compounds. The antioxidant properties or radical scavenging ability of sodium *N*-ethyl-*N*-phenyldithiocarbamate and its

Table 3 MIC results for the complexes and control drugs

Name	*Aspergillus flavus*	*Fasiparium oxysporium*	*Staphylococcus aureus*	*Pseudomonas aureginosa*	*Escherichia coli*	*Salmonella typhi*
NaL	100	100	100	100	100	100
[CoL$_2$]	–	–	<10	50	–	25
[CuL$_2$]	50	30	40	<10	20	50
[MnL$_2$]·0.25H$_2$O	30	–	–	–	25	15
[CrL$_3$]·2H$_2$O	25	<10	30	25	–	–
Streptomycin	–	–	<10	15	12	15
Ketoconazole	12	<10	–	–	–	–

Values (in µg/mL) represent the mean of two replications; streptomycin standard antibacterial agent, ketoconazole standard antifungal agent, "–" Not screened

Table 4 Antioxidant data for the ligand and its Cu(II) complex

Concentration (μg/mL)	NaL	[CuL_2]	Ascorbic acid*
100	18 ± 0.512	48 ± 0.610	57 ± 0.431
200	23 ± 0.704	51 ± 0.610	62 ± 0.863
300	34 ± 0.105	55 ± 2.194	63 ± 0.863
400	39 ± 0.110	60 ± 0.747	67 ± 0.932
500	42 ± 1.535	75 ± 1.220	87 ± 1.220

No of replicates = 3, *X* ± SEM

* Standard

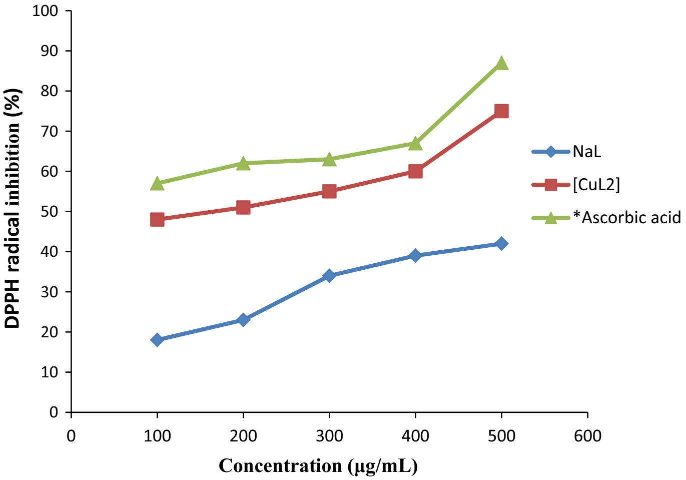


Fig. 7 Trends in the inhibition of the DPPH radical by the ligand and its Cu(II) complex with standard ascorbic acid at various concentrations

copper (II) complex is presented in Table 4 and compared to ascorbic acid (Fig. 7) which is a standard antioxidant drug. The DPPH scavenging activity of Cu(II) complex is significantly higher than that of the free ligand, indicating that this complex is a much better/stronger free radical scavenger and antioxidant than the ligand but lower when compared to ascorbic acid as a standard. Increase in the concentration of the compounds in the antioxidant studies resulted in a corresponding increase in the radical scavenging ability of the compounds.

Conclusion

Dithiocarbamate complexes of Co(II), Cu(II), Mn(II), Pd(II) and Cr(III) were successfully prepared and characterized using different techniques. Thermal studies showed a decomposition of the complexes into their respective metal sulphides, a good characteristic for precursor compounds used for metal chalcogenide nanoparticles and thin film synthesis. The ligand and metal complexes have been screened to determine their biological properties, including the antifungal and antibacterial activities under in vitro experimental conditions. The complexes showed moderate to good antimicrobial activity and, overall, a better antimicrobial activity than the free ligand due to chelation. The antioxidant activity of the ligand and its copper complex was studied by DPPH free radical scavenging methods. The ligand and the complex exhibited scavenging activity against DPPH free radicals but the complex showed a significantly higher property than that of the free ligand, indicating that this complex is a much better/stronger free radical scavenger and antioxidant agent. This indicates that it can be a promising active component in the field of biomedical application.

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