

Synthesis, spectroscopic characterization, antifungal and antibacterial studies of copper(II) dithiocarbamate complexes

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Abstract

We report the synthesis, spectroscopic characterization, antifungal and antibacterial studies of copper(II) dithiocarbamate complexes. The complexes were characterized by elemental analysis, UV-Vis, FTIR and ¹H NMR spectroscopy. The compounds were formulated as four coordinate species and FTIR spectra studies confirmed that the dithiocarbamate ligands act as bidentate chelating ligands around the copper ions. Electronic spectra studies indicate that the copper complexes are in a four coordinate square planar geometries. The antimicrobial potential of the complexes against four fungi and four bacteria isolates revealed minimum inhibitory concentrations (MIC) ranging from 0.03-0.050 mg/mL with [Cu(anidtc)₂] being the most active. The results indicates copper(II) complexes possessed broad spectrum antimicrobial activity that is better than that of Nystartin and Ketoconazole (standard antifungal drugs) and might lead to more promising metal complexes for the production of potent antimicrobial agents to manage the ever increasing antibiotic resistant bacteria and fungi.

Keywords: Copper(II), dithiocarbamates, spectroscopic characterization, antifungal, antibacterial.

1. INTRODUCTION

Transition metal dithiocarbamate complexes are known to have large scale biological effects with various applications as antifungals, herbicides and insecticides among many other medical applications [1]. They are also being studied for their use in agrochemicals, pharmaceuticals, intermediates in organic synthesis, as protecting group in peptide synthesis or as chelators in materials chemistry [2-4]. Dithiocarbamate ligands have extensive coordination chemistry and wide range of applications [5-9]. The fungicidal activity of dithiocarbamate of alkali, alkaline earth and transition metals has been known for a long time [10-19] and these complexes showed selective activities towards some of the test microorganisms. De lima *et al.* [7], reported the biological studies of some copper(II) dithiocarbamate and *in vitro* activities of all the complexes against colonies of *C. albicans*, *S. aureus* and *P. aeruginosa* indicates that the compounds showed promising activities against *C. albicans* and *P. aeruginosa*. Ferreira *et al.* [20] reported the synthesis, characterization and antimicrobial properties of new copper(II) DTC complexes. Despite the poor activity towards the tested bacteria, complexes were quite effective against the fungi species [20]. One advantage of copper-based antimicrobial compounds is multitoxicity, which renders copper effective against multiresistant germs like *Staphylococcus aureus* or carbapenemase-resistant bacteria. Copper and many of its alloys have been registered as antimicrobial materials [21]. A developing interest in the area of dithiocarbamate chemistry is the functionalization of the backbone such that new applications and interactions can be developed [21]. Dithiocarbamate compounds are widely used in agriculture as standard fungicides against variety of plant diseases [22-25] and are considered chemicals of low toxicity for humans [26-28]. Hence this study was designed to explore the antifungal and antibacterial activity of synthesised Cu(II) dithiocarbamate complexes against fungi and bacteria of medical importance. In this paper, we present the synthesis, characterization, antifungal and antibacterial studies of some copper(II) dithiocarbamate complexes.

2. EXPERIMENTAL

2.1 Material and Physical measurement

Piperidine, p-Anisidine, butyl amine, sodium hydroxide, carbon disulphide, diethyl ether and CuCl₂ were bought from Sigma-Aldrich and they were used as obtained. The NMR spectra for ligands was recorded using Bruker ultrashield 400 NMR spectrometer at frequencies 400.1 MHz for ¹H and 100.6 MHz for ¹³C nuclei. FT-IR study was carried out using Perkin Elmer FTIR-

2000; FTIR spectra were recorded in the range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹ as KBr pellets. The electronic spectra for both the ligands and complexes in solution were recorded using Perkin-Elmer Lambda 25 UV-Vis spectrometer. The samples were placed in quartz cuvettes of 1 cm path length.

2.2 Synthesis of sodium salt of dithiocarbamate ligands

Sodium hydroxide (2 g, 0.05 mol) dissolved in minimum amount of distilled water was allowed to attain an ice temperature, to this, cold carbon disulfide (3 mL, 0.05 mol) was added. This was then followed by the addition of anisidine, 6.1575 g; or butyl amine, 4.99 mL or piperidine, 5.00 mL (0.05 mol). The mixture was stirred for 2-3 h while keeping the temperature below 4 °C. A white product was then filtered and washed with ether.

2.3 Synthesis of metal complexes

The preparation of the complex was carried out at room temperature. About 15 mL aqueous solution of the CuCl₂ (0.107 g, 0.625 mmol), was added to 15 mL aqueous solution of anisidine, 0.27 g; butyl amine, 0.21 g and piperidine, 0.23 g (1.250 mmol), the green or brown precipitate which immediately forms was stirred for about 45 minutes to ensure complete reaction. The solid precipitate was filtered off, rinsed with distilled water and dried at ambient temperature.

[Cu(anidtc)₂]: yield = 1.81g, 60%. Selected IR, (cm⁻¹): ν(N-H) 3414.34, ν(C-N) 1506.47, ν(C-S) 1039.40, ν(M-S) 327.28. Anal. Calc. for C₁₆H₁₆N₂O₂S₄Cu (459.73): C, 41.80; H, 3.51; N, 6.09; S, 27.82. Found: C, 41.38; H, 3.70, N, 5.63; S, 27.55.

[Cu(butdte)₂]: yield = 1.13g, 53%. Selected IR, (cm⁻¹): ν(N-H) 3415.04, ν(C-N) 1507.21, ν(C-S) 916.61, ν(M-S) 327.69. Anal. Calc. for C₁₀H₂₀N₂S₄Cu (359.71): C, 33.39; H, 5.60; N, 7.79; S, 35.55. Found: C, 32.87; H, 5.70, N, 7.63; S, 35.75.

[Cu(pipdte)₂]: yield = 2.16g, 66%. Selected IR, (cm⁻¹): ν(C-N) 1506.32, ν(C-S) 994.07, ν(M-S) 327.60. Anal. Calc. for C₁₂H₂₀N₂S₄Cu (383.73): C, 37.56; H, 5.25; N, 7.30; S, 33.33. Found: C, 37.41; H, 5.70, N, 7.63; S, 33.55.

2.4 Antimicrobial susceptibility screening

20 mg each of the metal complex was dissolved in 5 mL of dimethyl sulfoxide (DMSO) to obtain final concentration of 2 mg/mL for the compounds. *Candida rugosa*, *Candida neoformans*, *Candida albicans* and *Trychophyton mucoides* were used to investigate the antifungal activity of the compounds, while *Escherichia coli*, *staphylococcus aureus*, *Salmonella typhi* and *S. typhimurium* were used for the antibacterial activity. These organisms were obtained from the Department of Biochemistry

and Microbiology, University of Fort Hare, South Africa, and were maintained on nutrient broth (Oxoid LTD, Basingstoke, Hampshire, England) for 24 hours before being used.

The MIC values for the compound against bacteria and fungi were determined by using two-fold serial microdilution method as described by Eloff [29]. Organisms were maintained on the nutrient agar at 4 °C in the refrigerator and were revived for bioassay by sub-culturing in fresh nutrient broth (Oxoid Ltd, Basingstoke, Hampshire and England) prepared in 20% DMSO for 24 hours before use. The inoculum size was adjusted to a final density of 10^6 ufl. This was used to inoculate 96-well microtitre plates containing serial two fold dilutions of the compounds (0.5 - 0.0039 mg/mL) under aseptic condition. The plates were incubated under aerobic conditions at 37 °C and examined after 24 h. 40 μ L of 0.2 mg/mL p-iodonitrotetrazolium (INT) (97% purity, Sigma, South Africa) solution was used as a bacterial growth indicator, this was added to each well and incubated for 30 min at 37°C. The change of the colour from being colourless to a red coloured product was taken as biological activities of organisms. Each treatment was performed in double and a complete suppression of growth at a specific concentration of an extract was required for it to be declared active [30, 31]. Pure distilled water and sample free solvents were use as controls. The same procedure was repeated for the antifungal testing only that the plates were incubated at 25°C unlike 37°C for the bacteria.

3. RESULTS AND DISCUSSION

3.1 Synthesis of ligands and complexes

The complexes were obtained after reacting each ligand with copper(II) chloride in a 2:1 mole ratio at room temperature as shown in Scheme 1. The complexes are formulated as a four coordinate species in which the dithiocarbamate ligand acts as a bidentate chelating ligand.

Different solvents were used to test the solubility of ligands and complexes. All ligands were soluble in water, therefore, water was used to synthesize the complexes. The complexes were all not soluble in water but soluble in some polar coordinating solvents such as DMF and some in DMSO.

3.2 Infrared spectra studies

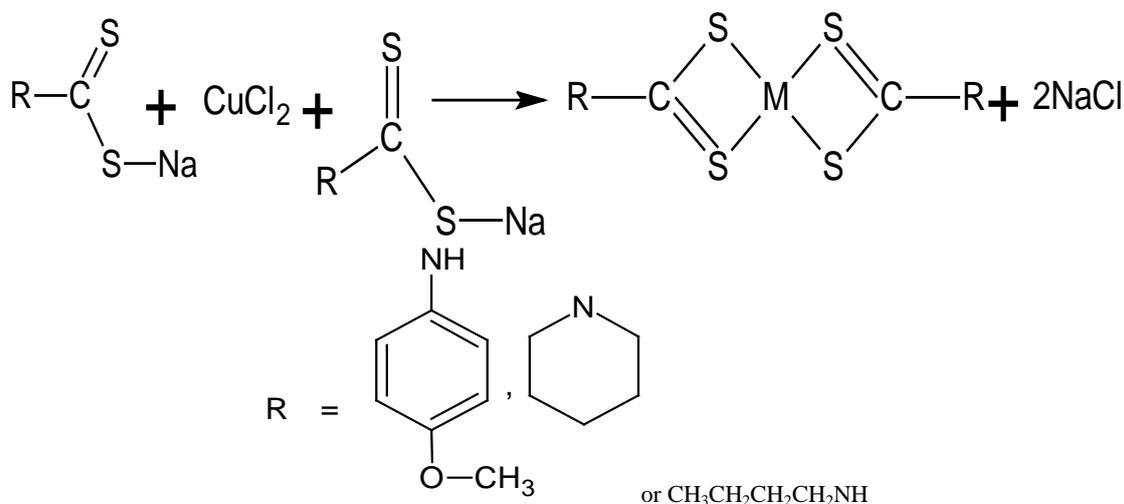
Three important bands are expected in the IR spectra of dithiocarbamate compounds. The first one is the band in the range 1550-1450 cm^{-1} corresponding to $\nu(\text{C-N})$ stretching vibrations

[32]. The second one is the vibration in the finger print region in the range 1060–940 cm^{-1} , associated with $\nu(\text{C-S})$ bands [33]. The third important band occurs at far infrared region and is associated with the $\nu(\text{M-S})$ vibration in the range 400–300 cm^{-1} [34]. The infrared spectra of the ligands and their corresponding complexes were compared and carefully assigned. In the anisdtc ligand, the $\nu(\text{N-H})$ which is due to the N-H bond of the amine was observed at 3414 cm^{-1} and there was no shift of this peak in the complex, this indicates that the N-H was not bonded to the metal ion.

In the anisdtc ligand, the $\nu(\text{C-N})$ stretching vibrations observed at 1548 cm^{-1} , this stretching vibration in butylidtc ligand was observed at 1506.69 cm^{-1} which shifted to 1507.67 cm^{-1} in the complex, the small shift of this peak that was observed in the complex might be due to the formation of the partial double bond confirming the formation of the complex [35], in pipdctc this peak was observed at 1468.39 cm^{-1} in the complex it also shifted to 1506.32 cm^{-1} . In the spectra of the ligands, two bands were observed for the $\nu(\text{C-S})$ symmetrical and asymmetrical stretching vibrations and these appeared as a single sharp bands in the spectra of all the complexes. This indicates that the dithiocarbamate ligands are bonded to the copper ions as bidentate chelating ligands [36]. The $\nu(\text{M-S})$ stretching vibrations appeared at 327 cm^{-1} , 327.69 cm^{-1} , and 327.60 cm^{-1} for $[\text{Cu}(\text{anisdtc})_2]$, $[\text{Cu}(\text{butylidtc})_2]$ and $[\text{Cu}(\text{pipdctc})_2]$ respectively.

3.3 Electronic spectra of copper (II) complexes and their ligands.

Tetrahedral compounds of copper (II) are not very common, but they usually have a single broad band in the visible region [38]. Copper dithiocarbamate complexes are known to show intense ligand-to-metal charge transfer transitions (LMCT) around 430 nm, as well as a large absorption around 640 nm based on the d-d transitions due to delocalized d-orbitals in the sulfur atoms of the dithiocarbamate ligands. In the complexes, bands below 300 nm are attributed to the intraligand transitions. Three absorption bands are expected in the electronic spectra of dithiocarbamate ligands, the first one is the intraligand $\pi \rightarrow \pi^*$ electronic transitions for the N-C=S and S-C=S group [39], and $n \rightarrow \pi^*$ occurring in the sulphur atoms. The other two expected transitions are metal ligand charge transfer transitions (LMCT) and the d-d transitions [34].



Scheme 1: Synthesis of copper(II) complexes.

Table 1: Antifungal activity of the compounds and standard antifungal drugs

Organism	Compound (mg/mL)				
	[Cu(anidtc) ₂]	[Cu(butdct) ₂]	[Cu(pipdct) ₂]	Nystartin	Ketoconazole
<i>Candida rugosa</i>	0.13	0.13	0.50	0.13	0.13
<i>Candida neoformans</i>	0.06	0.06	0.50	0.13	0.13
<i>Candida albicans</i>	0.03	0.06	0.50	0.25	0.13
<i>Trychophyton mucoides</i>	0.03	0.06	0.50	0.25	0.25

Table 2: Antibacterial activity of the compounds and standard antibiotics

Organism	Compound (mg/mL)				
	[Cu(anidtc) ₂]	[Cu(butdct) ₂]	[Cu(pipdct) ₂]	Strepto	Tetracy
<i>Escherichia coli</i>	0.06	0.25	0.50	0.02	0.01
<i>Staphylococcus aureus</i>	0.03	0.13	0.25	0.02	0.01
<i>Salmonella typhi</i>	0.03	0.06	0.25	0.02	0.01
<i>Salmonella typhimurium</i>	0.06	0.13	0.50	0.02	0.03

Strepto; Streptomycin, tetracy; Tetracycline

Detailed interpretations of the spectra of copper(II) ion are complicated because of the relatively low symmetry of the environments in which they are characteristically formed [40-42]. Almost all copper (II) compounds are blue or green due to an absorption band in the region 600-900 nm and these bands are usually unsymmetrical and arise from several overlapping transitions due to Jahn Teller distortion. Their definitive resolution into the different number of sub-bands is extremely difficult and almost impossible. Exceptions are due to charge transfer transitions that could make the compounds to appear red or brown [40]. In octahedral copper(II) complexes, a single absorption band is expected in the visible region [43]. These bands are due to several overlapping bands [40, 44]. A regular tetrahedral copper(II) complexes will show a single broad band located near the IR region while the copper(II) complexes in square planar environment show two bands in the visible region. The electronic spectrum of [Cu(anisidtc)₂] showed two broad bands at 389 nm and 570 nm ascribed to the d-d transitions for a Cu(II) ion in a square planar crystal field. These transitions are assigned to ²B_{1g}→²A_{1g} and ²B_{1g}→E_g transitions [40]. The bands in the 370-396 nm are assigned to metal to ligand charge transfer transitions. The other bands observed were due to intraligand transitions of the N-C=S and S-C=S groups of the ligand. In the electronic spectrum of [Cu(butylidtc)₂], two bands were observed in the visible region at 446 and 651 nm attributed to the d-d transition of a square planar Cu(II) complex. The electronic spectrum of the [Cu(pipdct)₂] showed two broad bands at 414 and 579 nm assigned to the d-d transitions of a copper(II) ion in a square planar geometry. There is a shoulder at 348 nm which is assigned to metal to ligand charge transfer. The other bands observed were due to intra ligand charge transfer transitions from π→π* and n-π* from the N-C=S and S-C=S groups.

3.4 NMR spectra studies

In the NMR spectra of the ligands, all the chemical shifts were found in the expected regions. The ¹³C NMR for all ligands showed all the expected chemical shifts for the ligands. The ¹H NMR spectrum for anisidine dithiocarbamate ligand (anisidtc) showed the CH₃ from O-CH₃ as a singlet at 1.28 ppm, while =CH from the aromatic ring appeared as a doublet around 6.95-6.94 ppm. There was an extra quartet that might be due to the impurities. ¹³C NMR spectrum showed the resonance at 181.05 ppm which was assigned to δ(N¹³CS₂) of NCS₂ moiety. The signals observed at 114.77 ppm and 127.52 ppm were assigned to the C=C bond in the aromatic ring. The spectrum also showed signals for C-N bond from CNH group in the ligand and the C-O bond from the OCH₃ group of the ligand at 55.52 and 77.22 respectively. There was only one extra peak at 158 ppm which is assumed to be due to the impurities of the ligand. The butyl amine dithiocarbamate ligand (butylidtc) ¹³C NMR spectrum showed the

δ(N¹³CS₂) resonance at 214.50 ppm. The spectrum also exhibits the signals around 13.54-14.30 ppm that are due to the CH₃ group. The signals around 19.65-20.24 ppm were assigned to the two CH₂ groups. While the signal that appeared around 40.17 ppm was assigned to the C-N bond. ¹³C NMR spectrum of piperidine dithiocarbamate ligand (pipdct) exhibited the δ(N¹³CS₂) resonance at 212.87 ppm. The signal that was due to the C-N bond from the ring appeared at 50.78 ppm. The two different CH₂ showed their signals around 24.81-26.20 ppm and 39.51-40.34 ppm.

3.5 Antifungal and antibacterial studies

The antifungal activity of each compound was measured *in vitro* against *Candida rugosa*, *Candida neoformans*, *Candida albicans* and *Trychophyton mucoides* microorganisms. The minimum inhibitory concentration (MIC) of the compounds against each of the four organisms is shown in Tables 1. MIC is defined as the lowest concentration able to inhibit any visible fungal growth on the culture plates [45]. [Cu(anidtc)₂] and [Cu(butdct)₂] inhibited *Candida rugosa* at the concentration of 0.031 mg/mL which compared favourably with Nystratin and Ketoconazole (Standard antifungal drugs). These two compounds were more potent than the two antifungal drugs against *Candida neoformans* and *C. albicans* by inhibiting these organisms at the MIC of 0.03 and 0.06 mg/mL respectively while it was 0.25 mg/mL in Nystartin and Ketoconazole.

The compounds were further screened against four bacteria isolates *Escherichia coli*, *Staphylococcus aureus*, *Salmonella typhi* and *Salmonella typhimurium*. The result is presented in Table 2. All the compounds inhibited both the Gram positive bacteria *Staphylococcus aureus* and the three Gram negative bacteria strains at minimum inhibitory concentration (MIC) ranging from 0.03-0.50 mg/mL with [Cu(anidtc)₂] being the most active compound in comparison to the other two complexes against the bacterial isolates and [Cu(pipdct)₂] again is the least active compound against all the test bacteria strains.

4. CONCLUSION

Copper(II) complexes of three dithiocarbamate ligands were synthesized and characterized by elemental analysis, conductivity measurements, UV-Vis and FTIR spectroscopy and the ligands were further characterize by ¹H NMR. The complexes were formulated as four coordinate species in which the metal ions are coordinated to two molecules of dithiocarbamate ligands through the sulfur atoms acting as bidentate chelating ligands. Electronic spectra studies confirmed that the complexes are in square planar geometries and the bidentate chelating modes of the dithiocarbamate ligands were confirmed with FTIR spectra studies. The copper complexes were evaluated against four fungi and four bacterial isolates to determine their antifungal and antibacterial activities. The minimum inhibitory concentrations of

the complexes against the fungi and bacterial isolates are between 0.03 and 0.50 mg/mL with [Cu(anidtc)₂] being the most active. The results obtained from this study showed that Cu(II) dithiocarbamate complexes possessed broad spectrum antimicrobial activities.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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