

Synthesis, Spectroscopic Characterization and Preliminary Antimicrobial Studies of Mn(II) and Cu(II) Complexes of two Thiolates; *S,S'*-(2,6-Diaminopyridine-3,5-diyl) Dibenzenecarbothioate (DBCT) and *S*-Benzyl Benzenecarbothioate (BBCT)

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Abstract: *S,S'*-(2,6-Diaminopyridine-3,5-diyl)dibenzenecarbothioate was formed by condensing 2,6-diamino-3,5-dithiopyridine and benzoyl chloride in the presence of pyridine. Also *S*-benzyl benzenecarbothioate was prepared by the condensation of benzoyl chloride and phenylmethanethiol in the presence of pyridine. The complexes of these compounds were prepared using copper(II) and manganese(II) chloride salts. The thiolates were characterized on the basis of their electronic, infrared and NMR spectra whereas the complexes were characterized via electronic and infrared studies. The IR spectral studies indicate that the ligands coordinated through the carbonyl oxygen, the sulphur atom and also with the amino group in DBCT. Antimicrobial studies on the ligands and their complexes showed varying degrees of inhibition on the growth of the following microorganisms; *Staphylococcus aureus* (ATCC 25923), *Pseudomonas aeruginosa* (ATCC 27853), *Bacillus subtilis* (ATCC 6633) and *Candida albicans* (ATCC 2091). The compounds showed no activity against *Escherichia coli* (ATCC 25922).

Keywords: Complexes, IR, NMR Spectra, Synthesis.

Introduction

Ligands containing and coordinating through sulphur atoms have attracted much attention. This is due to their efficacy in metal chelation therapy¹, in anti-influenza, antiprotozoan,

antibacterial and antiviral treatment². Some of them have also been indicated to have high potency as fungicides³ and pesticides⁴. Recently 4-aminoantipyrine thiosemicarbozones^{2,5} and their Co(II), Ni(II) and Cu(II) complexes were synthesized, characterized and found to have strong antifungal activity and comparative antibacterial activity with ampicillin and tetracycline. The recent discovery of acireductone dioxygenase (ARD), a metalloenzyme with Ni(II) centre having the capacity to catalyse the oxidative breakdown of acireductone to 2-methylthiopropionate in *Klebsiella pneumoniae*⁶, has fuelled interest in compounds having sulphur donor atoms.

Research into inorganic pharmaceuticals is gaining currency due to the drive for new chemotherapeutic agents that can combat bacterial infections. At present infections caused by bacteria constitute a serious burden to healthcare systems world wide. Antibiotic resistant strains of bacteria are an increasing threat to animal and human health, with resistance mechanisms having been described for virtually all known antimicrobials currently available for clinical use. A way of overcoming antibiotic resistance of pathogenic microorganisms is by using new compounds that are not based on existing synthetic antimicrobial agents⁷.

In this work we have synthesized two new ligands: *S,S'*-(2,6-diaminopyridine-3,5-diyl) dibenzenecarbothioate (DBCT) and *S*-benzyl benzenecarbothioate (BBCT) having C-S bonds. We have also prepared their Mn(II) and Cu(II) complexes and characterized them via UV, IR and Conductance measurements. In addition, the ligands were characterized by NMR spectral studies as well as elemental analysis. The ligands and complexes were further investigated for their antimicrobial activities against some bacteria and fungus. The results suggest great potential for these ligands and complexes as antibacterial and antifungal agents.

Experimental

Manganese(II) chloride and copper(II) chloride were products of Fluka, Switzerland, Benzoyl chloride, Phenylmethanethiol and 2,6-diaminopyridine-3,5-dithiol were obtained from BDH, England and were used as supplied unless otherwise stated. UV Visible spectra of the ligands and complexes were obtained on CECIL CE 9050 Spectrophotometer. FTIR spectra of the compounds were run as Nujol mulls on Buck scientific model 500 FTIR Spectrometer. ¹³C and ¹H NMR spectra were recorded on YH 200 MHz Varian Mercury NMR Spectrometer using DMSO and CDCl₃ as solvents respectively. The ¹H NMR Peaks were observed at about 200 MHz and ¹³C NMR spectra were observed at about 50 MHz. Elemental analysis was done using LECO-CHNS 932 Microanalysis apparatus at Department of Pharmaceutical Sciences, University of Strathclyde, Glasgow. Conductance measurements for the compounds were made at 28 °C using CD 600 Milwaukee Conductivity meter with a cell constant 1.0 cm⁻¹. Standard solutions were prepared in nitrobenzene. Molecular weights of the ligands and complexes were determined cryoscopically based on the depression of melting point of camphor as reported elsewhere⁸. All other reagents were of analytical grade and were used as supplied.

Synthesis of *S,S'*-(2,6-diaminopyridine-3,5-diyl)dibenzenecarbothioate (DBCT)

5.8 mL (0.05 mole) of benzoyl chloride, 2.925 g (0.025 mole) 2,6-diaminopyridine-3,5-dithiol and about 5 mL of pyridine were stirred in a round-bottomed flask until evolution of HCl ceased. Then 2 mL of distilled water and about 2 mL of pyridine were added to eliminate any excess of the reagents. Pale green solid separated and was recrystallized with dilute ethanol. The yield was 66%.

Synthesis of *S*-ben

2.9 mL (0.025 mole) 2,6-diaminopyridine-3,5-dithiol and about 5 mL of pyridine were stirred in a round-bottomed flask until evolution of HCl ceased. Then 2 mL of distilled water and about 2 mL of pyridine were added to eliminate any excess of the reagents. Pale green solid separated and was recrystallized with dilute ethanol. The yield was 66%.

Synthesis of Mn(II)

1.98 g (0.01 mole) Mn(II) chloride and about 10 mL of absolute ethanol were stirred in a round-bottomed flask and the solution was allowed to cool and was recrystallized with absolute ethanol. The yield was 66%.

Also BBCT was synthesized for DBCT. The green crystals were obtained after 120 hours. The yield was 66%.

Synthesis of Cu(II)

7.62 g (0.02 mole) Cu(II) chloride and about 10 mL of absolute ethanol were stirred in a round-bottomed flask and refluxed until the solution was separated. It was filtered and dried.

Following above procedure, Cu(II) chloride was synthesized. The crystals were obtained after 120 hours. The yield was 66%.

Antimicrobial properties

The antimicrobial properties of the ligands and complexes were determined against *Pseudomonas aeruginosa* (ATCC 27853), *Candida albicans* (ATCC 9001), *Staphylococcus aureus* (ATCC 29212) and *Escherichia coli* (ATCC 8739). The suspensions were prepared in 0.1 mL of three hours old broth. The suspensions were then inoculated into 2.5 mm deep wells in 20 mg/mL dimethyl sulfoxide (DMSO) containing agar. The wells were labeled 1 to 6 and left on the lab bench at 37 °C for 24 hours. The plates were then read and the results were based on the measure of zone of inhibition. The experiment was repeated three times and the whole millimeter.

Results and Discussion

The reaction of benzoyl chloride with 2,6-diaminopyridine-3,5-dithiol

Synthesis of *S*-benzyl benzenecarbothioate (BBCT)

2.9 mL (0.025 mole) benzoyl chloride, 2.33 mL (0.025 mole) Phenylmethanethiol and about 5 mL of pyridine were mixed in a 500 mL round-bottomed flask. The mixture was heated with stirring over a water bath until HCl fume ceased. Then about 2 mL of distilled water and about 2 mL of pyridine were added to eliminate excess reagent. The mixture was allowed to cool and white needle like crystals separated. The product was recrystallized with absolute ethanol. The yield was 87.9%.

Synthesis of Mn(II) complex of DBCT and BBCT

1.98 g (0.01 mole) $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 7.62 g (0.02 mole) DBCT were dissolved separately in about 10 mL of absolute ethanol. The two solutions were mixed in a 500 mL round-bottomed flask and refluxed for 1 h under constant stirring at 50 °C. The resulting greenish solution was allowed to cool after which a pale green crystals separated. They were filtered, washed with ethanol and dried *in vacuo* in a desiccator over CaCl_2 .

Also BBCT was reacted with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in the ratio of 2:1 following the method adopted for DBCT. The green solution formed was allowed to cool. Needle-like white crystals separated after 120 hours. The crystals were washed with ethanol and dried *in vacuo* over CaCl_2 .

Synthesis of Cu(II) complexes of DBCT and BBCT

7.62 g (0.02 mole) DBCT and 1.705 g (0.01 mole) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved separately in about 10 mL of absolute ethanol. The two solutions were mixed in a 500 mL round-bottomed flask and refluxed under constant stirring for 1 h at 50 °C. After cooling a pale green solid separated. It was filtered, washed with ethanol and dried *in vacuo* over CaCl_2 .

Following above procedure, 4.56 g (0.02 mole) BBCT was reacted with 1.705 g (0.01 mole) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The solution was allowed to cool and shiny white crystals separated after 72 h. The crystals were filtered, washed with ethanol and *in vacuo* over CaCl_2 .

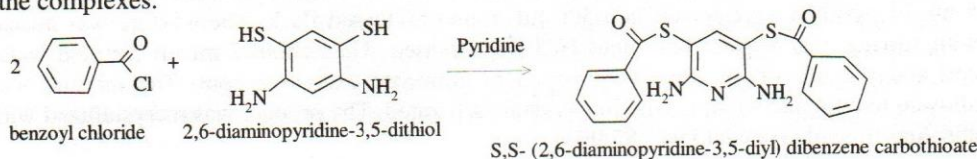
Antimicrobial properties

The antimicrobial properties of DBCT, BBCT and their Mn(II) and Cu(II) complexes were determined against *Staphylococcus aureus* (ATCC 25923), *Bacillus subtilis* (ATCC 6633), *Pseudomonas aeruginosa* (ATCC 27853), *Escherichia coli* (ATCC 25922) and *Candida albicans* (ATCC 2091) using the agar-well diffusion method⁹. Each Mueller-Hinto agar (and sabouraud dextrose agar for *Candida albicans*) plate was inoculated with 0.1 mL of three hours broth culture of each test organism. Wells (7 mm in diameter and 2.5 mm deep) were cut into the inoculated agar and labeled from one to seven. 50 μL of 20 mg/mL dimethylsulfoxide solution (DMSO) of DBCT, BBCT, $[\text{Mn}(\text{DBCT})\text{Cl}_2]$, $[\text{Mn}(\text{BBCT})_2(\text{H}_2\text{O})_2]^{2+}$, $[\text{Cu}(\text{BBCT})_2\text{Cl}_2]$ and $[\text{Cu}(\text{DBCT})\text{Cl}_2]$ respectively were placed in wells labeled 1 to 6 and 20% v/v DMSO was delivered into the 7th well. The set up was left on the lab bench for one hour for the solutions and DMSO to diffuse into the media. The plates were then incubated at 37 °C for 24 h. Assessment of antimicrobial activity was based on the measurement of the diameter of inhibition zone (IZD) around the wells. The experiment was replicated three times and the mean IZD was recorded to the nearest whole millimeter.

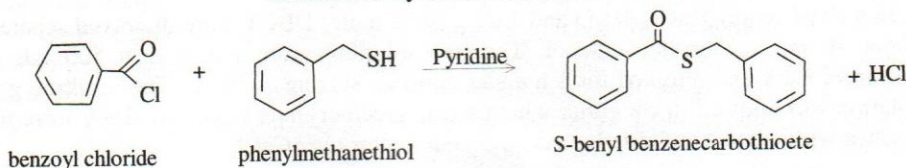
Results and Discussion

The reaction of benzoyl chloride with 2,6-diaminopyridine-3,5-dithiol afforded *S,S'*-(2,6-diaminopyridine-3,5-diyl)dibenzenecarbothioate according to Scheme 1. Also the reaction of

phenylmethanethiol with benzoyl chloride yielded *S*-benzyl benzenecarbothioate as seen in Scheme 2. Reactions of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ separately with the ligands afforded the complexes.



Scheme 1. Synthesis of DBCT



Scheme 2. Synthesis of DBCT

Some physical data of the ligands and complexes are presented in Table 1 while Table 2 gives the elemental data of the ligands. There is close agreement between what is expected and what was determined. The crystalline solids were found to be stable and on storage for about 12 months their nature did not change. The molar conductance values suggest the complexes to be most probably non-electrolytes as there is no appreciable dissociation except $[\text{Mn}(\text{BBCT})_2(\text{H}_2\text{O})_2]^{2+}$ which is most likely a 2:2 electrolyte².

Table 1. Some physical data of the ligands and complexes

Compound	% Yield	Colour	Melting point, °C	$\Omega\text{m}, \text{ohm}^{-1} \cdot \text{cm}^2 \text{mole}^{-1}$
DBCT	66	Pale green	178-180	-
BBCT	88	White	115-117	-
$[\text{Cu}(\text{DBCT})\text{Cl}_2]$	75	Green	287-290	8.52
$[\text{Cu}(\text{BBCT})_2\text{Cl}_2]$	62	White	133-135	8.72
$[\text{Mn}(\text{DBCT})\text{Cl}_2]$	68	Dirty green	291-292	12.01
$[\text{Mn}(\text{BBCT})_2(\text{H}_2\text{O})_2]^{2+}$	79	Shiny white	108-110	57.60

Table 2. Analytical data of the ligands

Compd	Molecular mass		%C		%H		%N		%S	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
DBCT	381.48	379.98	59.82	62.46	3.96	4.38	11.02	10.89	16.81	18.12
BBCT	228.31	230.01	73.65	71.80	5.30	6.10	-	-	14.04	13.81

Job's continuous variation method and slope ratio method respectively were employed in the determination of the composition of the complexes. $[\text{Cu}(\text{BBCT})_2\text{Cl}_2]$ was analyzed at 337 nm, $[\text{Mn}(\text{DBCT})\text{Cl}_2]$ at 247 nm, $[\text{Cu}(\text{DBCT})\text{Cl}_2]$ at 343 nm and $[\text{Mn}(\text{BBCT})_2(\text{H}_2\text{O})_2]$ at 247 nm. The results indicate 1:1 metal to ligand ratio for the complexes of DBCT and 1 metal to ligand ratio for the BBCT complexes. The results could be interpreted to mean generalized MLX_2 octahedral complexes of DBCT with Mn(II) and Cu(II) where DBCT is tetradentate and ML_2X_2 octahedral complexes of BBCT where BBCT is bidentate. DBCT coordinates to the metal through S, O or N atoms. BBCT is limited to the O and S atoms for ligation

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Electronic spectra

DBCT shows a strong absorption at 247 nm and BBCT absorption was observed at 258 nm in the UV. These results as seen in Table 3 are likely due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the ligand molecules. The spectrum of $[\text{Cu}(\text{DBCT})\text{Cl}_2]$ and $[\text{Cu}(\text{BBCT})_2\text{Cl}_2]$ are similar showing new peaks at 337 nm (29656 cm^{-1}) and at 343 nm (29172 cm^{-1}) respectively. These bands are likely due to metal to ligand charge transfer. The same deduction was made for Cu(II) complexes^{5,10}. The bands at 883 nm for $[\text{Cu}(\text{BBCT})_2\text{Cl}_2]$ and 886 nm for $[\text{Cu}(\text{DBCT})\text{Cl}_2]$ are attributed to a distorted octahedral geometry in the copper complexes. It has been reported that $d \rightarrow d$ transitions in copper complexes around 600 nm and 900 nm are indicative of a square pyramidal arrangement or a pseudo-octahedral environment with weak axial interaction for the Cu(II) complex¹¹. The spectrum of the Mn(II) complexes shows a shift to lower energies all centered between 224 nm to 247 nm. The shift to low wavelengths is probably the result of weak interaction between the ligands and Mn(II) or due to weak interaction between solvent molecules and the metal ions.

Table 3. Electronic spectral data (nm) of compounds

Compound	1, λ_{max}	2, λ_{max}	3, λ_{max}
DBCT	247	-	-
BBCT	258	-	-
$[\text{Cu}(\text{DBCT})\text{Cl}_2]$	247	337	886
$[\text{Cu}(\text{BBCT})_2\text{Cl}_2]$	248	343	883
$[\text{Mn}(\text{DBCT})\text{Cl}_2]$	247	247	894
$[\text{Mn}(\text{BBCT})_2(\text{H}_2\text{O})_2]^{2+}$	247,242	235,224	-

Infrared spectral data

The infrared absorption frequencies of the ligands and their complexes are displayed in Tables 4 and 5. In Table 4, the broad absorption peaks between 3457 cm^{-1} and 3416.22 cm^{-1} indicates N-H vibration. The peaks at about 2900 cm^{-1} - 2300 cm^{-1} have been assigned to C-H stretching vibration. There are no bands between 2700 cm^{-1} - 2500 cm^{-1} . This is indicative of absence of thiol (SH) bands^{12,13}, this shows that the ligands were formed as proposed by the clipping of the S-H bonds of the thiols to give $-\text{S}-\text{C}=\text{O}$. A comparison of the IR data of DBCT with that of the complexes as regards the N-H band shows that for $[\text{Cu}(\text{DBCT})\text{Cl}_2]$ there was little or no shift in its band but that of $[\text{Mn}(\text{DBCT})\text{Cl}_2]$ shifted to lower frequency of 3416.22 cm^{-1} indicating ligation to Mn through H_2N - but no coordination to Cu through the amino group. Another significant absorption is that of C=O which is centered at 1690.97 cm^{-1} in the ligand but shifted to 1630.08 cm^{-1} in the copper complex indicating possible coordination to the metal through the carbonyl group. However in the manganese complex, the strong peak at about 1695 cm^{-1} remained but with emergence of a new weak band at 1621.47 cm^{-1} indicating a remote possibility of ligation through the carbonyl group to manganese. The C-S bands showed up between 760 cm^{-1} and 690 cm^{-1} . The bands remain virtually unchanged in the manganese complex but shows some degree of shift in the copper complex suggesting coordination to the copper centre through the sulfur and non-ligation to the manganese ion through sulfur¹¹.

In Table 5, the IR spectra of the BBCT ligand is comparable to those of the complexes. One significant feature is the appearance of broad band at 3441.40 cm^{-1} in the Mn(II) complex. This has been ascribed to the presence of coordinated water in the complex. The carbonyl bands in the ligand are centered between 1700 cm^{-1} to 1669.26 cm^{-1} .

Table 4. IR spectral data (cm^{-1}) of DBCT and its Cu(II) and Mn(II) complexes

DBCT	[Cu(DBCT)Cl ₂]	[Mn(DBCT)Cl ₂]	Assignment
3455(br)	3457.86(br)	3416.22(br)	
	3156.46(sh)		ν (N-H)
2853.19(s)	2900(s)	2850(s)	ν (C-H)
2800 (s)	2853.35(s)	2900 (s)	
1694.97 (s)	1630.08(w)	1695.04(s)	ν (C=O)
		1621.47(w)	
1461.62(s)	1462.24(s)	1495(s)	ν (C-C) ring
1377.30(s)	1378.03(s)	1320(s)	
1289.10 (w)	1262.38(w)	1287.52(s)	ν (C-N)
1255 (w)	1036.40(w)	1027.40(w)	
1125.80(w)			
760(w)	755(w)	760(w)	
710.40(s)	718.36(m)	710.95 (s)	ν (C-S)
690.09(w)			
547.05(w)	527(w)	560.80(w)	ring breathing
	450.80(w)	458.50(w)	ν (M-O)
	410.20(w)	414.26(w)	ν (M-N)

s = strong, m = medium, sh = shoulder, w = weak.

Table 5. IR spectral data (cm^{-1}) of BBCT and its Cu(II) and Mn(II) complexes

BBCT	[Cu(BBCT) ₂ Cl ₂]	[Mn(BBCT) ₂ (H ₂ O) ₂] ²⁺	Assignment
		3441.40(br)	ν (H ₂ O)
2918.84(s)	2918.92(s)	2917(s)	ν (C-H)
2858.64(s)	2669.11(w)	2671(w)	
1700 (w)	1788.80(w)	1787.12(w)	ν (C = O)
1669.26(w)	1696.21(s)	1695.75(w)	
1650(w)	1582.07 (s)	1602 (w)	ν (C = C)
1453.03 (s)	1498.32 (s)	1450.88(s)	
1400 (m)	1377.32(s)	1377.18(s)	δ (ring)
1325(m)	1287.90 (m)	1287.23(s)	ω (CH ₂)
1215 (w)	1102.01(m)	1177.01(m)	δ (CH ₂) ring vibration
1127.08(m)	1018.21(m)	1071.42 (m)	
1069.69(m)			
999.89(m)	999.39(m)	918.34 (m)	ω (C-H) and
914.09(s)	915.73 (s)		ω (H ₂ O)
804.45(s)	805.49(m)	807.9(m)	ν (C-S)
706.83(s)	710.42(s)	710.89(s)	
537.50 (s)	549.31(s)	546.76(m)	γ (C-C)
			Ring vibration
	476.10(m)	457(w)	ν (M-O)
	320 (m)	325 (w)	ν (M-S)

These bands appear at about 1696 cm^{-1} in the complex as only one peak. The other medium peak at 1669.26 cm^{-1} in the ligand is completely missing in the complexes. This is indicative that the ligand coordinate to the metal ions through the carbonyl groups. Shifts,

weakening or absence of peaks of ligands on coordination to metal had been interpreted in terms of coordination through such functional group^{15,16}. The C-S band appeared at about 710 cm⁻¹-807 cm⁻¹ in the ligand and complexes. The peak at 706.83 cm⁻¹ in the ligand shifted to 710.89 cm⁻¹ in the Cu(II) and Mn(II) complexes respectively indicating possible ligation to the metal centres through the sulfur atom.

In the IR spectra of the complexes of both ligands, new bands having weak to medium intensities at 476 cm⁻¹ to 320 cm⁻¹ abound. These peaks are most probably metal to ligand bands (M-O, M-Cl, M-S and M-N). the same assertions had been adopted for some metal(II) complexes of 4-formylazohydrazoaniline antipyrine¹⁴ and aminoantipyrine thiosemicarbazone^{2,5}.

The IR data of the ligands and complexes generally imply that the DBCT is tetradentate coordinated from S, N-H₂ or C=O while BBCT is bidentate coordinating through S and C=O. The complexes of DBCT are likely octahedral complexes of the form MLX₂ (M=Mn(II) or Cu(II), L= DBCT and X=Cl). BBCT complexes are presented as [MnL₂(H₂O)₂]X₂ and [CuL₂X₂] (L= BBCT, X=Cl).

NMR data of ligands

A close look on the spectrum of this ligand, DBCT shows absence of peak around 3.5-3.8 ppm indicating non-existence of the -SH group in the ligand and confirming the condensation reaction forming the thiocarbonyl group to have taken place. The peak at 7.95 ppm is due to ten aromatic protons on the two side rings. The singlet at 7.52 ppm is due to the pyridine ring while the four -NH₂ protons on the pyridine have their bands at 7.6 ppm. In BBCT, the five aromatic protons on ring A appear at 7.8 ppm while the five protons on ring B have their peak centered at 7.5 ppm. The CH₂-S peak appeared as a singlet at 2.5 ppm.

The ¹³CNMR data of the ligands are much as expected as seen in Table 7. For DBCT, the ten aromatic carbons on the A and B symmetrical rings appear between 129.271 ppm and 131.411 ppm. Assignments have been given based on their proximity to the -C=O substituent and possible shielding effects¹¹. The carbons on the pyridine ring were presented on three peaks appearing between 131.411 ppm and 133.621 ppm. Appropriate assignments have been given based on degree of shielding or shielding provided by the hetero nitrogen and the sulphur atoms attached to the ring.

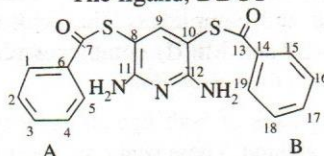
In the BBCT, nine peaks were observed. The CH₂ carbon peak appeared at 40.000 ppm. The carbon atoms on both aromatic rings showed some level of chemical equivalence hence assignments were done taking cognizance of this. C₆ and C₉ were distinct based on their nearness to C=O and S-CH₂ respectively and this showed relatively downfield peaks at 133.482 ppm and 133.328 ppm respectively.

Table 6. ¹H NMR data of ligands (ppm)

DBCT	
Peaks, ppm	Assignment
7.95 (10 H, m)	aromatic protons on the side rings.
7.52 (1 H, s)	proton in the middle pyridine ring.
7.6 (4 H, s)	protons on the two amino groups of the pyridine ring.
BBCT	
Peaks, ppm	Assignment
7.8 (5 H, m)	Aromatic protons on ring A
7.5 (5 H, m)	Aromatic protons on ring B
2.5 (2 H, s)	CH ₂ - S Protons.

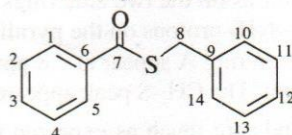
Table 7. ^{13}C NMR data of the ligands

The ligand, DBCT



Peaks for DBCT (ppm)	Assignments
129.271	C ₁ , C ₁₅
129.931	C ₂ , C ₁₆
129.472	C ₃ , C ₁₇
129.962	C ₄ , C ₁₈
129.986	C ₅ , C ₁₉
129.992	C ₆ , C ₁₄
131.411	C ₉
133.581	C ₈ , C ₁₀
133.621	C ₁₁ , C ₁₂
168.017	C ₇ , C ₁₃

The ligand, BBCT



Peaks for BBCT (ppm)	Assignment
40.0	C ₈
129.188	C ₂ , C ₁₁
129.224	C ₁ , C ₁₀
129.977	C ₃ , C ₁₂
130.011	C ₄ , C ₁₃
131.449	C ₅ , C ₁₀
133.328	C ₉
133.482	C ₆
168.063	C ₇

Antimicrobial properties

Antimicrobial properties of DBCT, BBCT and their Mn(II) complexes are presented in Table 8. As shown in the Table, the ligands and their metal complexes did not inhibit the growth of *E. coli* strain used in the study. $[\text{Cu}(\text{DBCT})\text{Cl}_2]$ showed activity only on *S. aureus* and *B. subtilis* while $[\text{Cu}(\text{BBCT})_2\text{Cl}_2]$ showed some level of activity against *S. aureus*, *B. subtilis*, *P. aeruginosa* and *C. albicans*. Also $[\text{Mn}(\text{BBCT})_2(\text{H}_2\text{O})_2]^{2+}$ was active against *S. aureus*, *P. aeruginosa* and *C. albicans* while $[\text{Mn}(\text{DBCT})\text{Cl}_2]$ showed activity only against *B. subtilis*. Generally, complexing the metals with the ligands did not show any marked enhancement of activity of the ligands. The significant exception is $[\text{Cu}(\text{BBCT})_2\text{Cl}_2]$ which has activity against *B. subtilis* whereas BBCT showed insensitivity to the microorganism. The results show that the ligands and some of their complexes could be exploited as potential source of chemotherapeutic agents.

Table 8. Antimicrobial properties of DBCT, BBCT and their metal complexes

Mean Inhibition Zone Diameter (IZD) (\pm sem)*						
Microorganism	DBCT	BBCT	[Cu (DBCT)Cl ₂]	[Cu (BBCT) ₂ Cl ₂]	[Mn (DBCT)Cl ₂]	[Mn(BBCT) ₂ (H ₂ O) ₂] ²⁺
<i>Staphylococcus Aureus</i> (ATCC 25923)	16 \pm 0.02	20 \pm 0.20	12 \pm 0.05	14 \pm 0.02	0	15 \pm 0.04
<i>Bacillus Subtilis</i> (ATCC 6633)	13 \pm 0.02	0	12 \pm 0.02	14 \pm 0.05	12 \pm 0.03	0
<i>Pseudomonas aeruginosa</i> (ATCC 27853)	10 \pm 0.01	11 \pm 0.00	0	11 \pm 0.03	0	12 \pm 0.02
<i>Escherichia coli</i> (ATCC 25922)	0	0	0	0	0	0
<i>Candida albicans</i> (ATCC 90028)	12 \pm 0.04	12 \pm 0.05	0	12 \pm 0.04	0	12 \pm 0.02

* mean of three replicates (measured in mm)

Conclusion

Two thiolates and their Mn(II) and Cu(II) complexes have been successfully prepared and characterized. The complexes presented an octahedral geometry although the copper complexes were identified as having distorted octahedral geometry. All the complexes were non-electrolytes except [Mn(BBCT)₂(H₂O)₂]²⁺ which crystallized as a 2:2 electrolyte. BBCT coordinate as a bidentate ligand whereas DBCT coordinate as a tetradentate ligand. The ligands and complexes showed good potential as prospective chemotherapeutic agents.

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