



Synthesis, Characterization and Biological Studies of S-1,3-Benzothiazol-2-ylthiophene-2-carbothioate and Its Ce(IV) and Nd(III) Complexes

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S-1,3-Benzothiazol-2-ylthiophene-2-carbothioate (SBC) was synthesized by the S-acylation of 2-mercaptobenzothiazole with thiophene-2-carbonylchloride in the presence of pyridine. Its Ce(IV) and Nd(III) complexes were also synthesized. The ligand and its Ce(IV) and Nd(III) complexes were characterized by UV-visible, IR and GC-MS spectroscopy. In addition, the ligand was characterized based on its ^1H and ^{13}C NMR data and the metal complexes based on conductivity measurement and stoichiometric ratio of combination. The infrared spectral study of S-1,3-benzothiazol-2-ylthiophene-2-carbothioate and its Ce(IV) and Nd(III) complexes gave evidence for coordination through the nitrogen of the benzothiazole ring and carbonyl oxygen. All the complexes were found to contain coordinated water and were assigned octahedral geometry. Antibacterial screening of the compounds were carried out *in vitro* on Gram-positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*). The compounds showed significant activities against Gram-positive bacteria than Gram-negative bacteria. However, the ligand showed more chemotherapeutic efficacy than the complexes. The compounds were not active against *Pseudomonas aeruginosa*.

Keywords: S-1, 3-Benzothiazol-2-ylthiophene-2-carbothioate, Ce(IV) and Nd(III) complexes, Antimicrobial activity.

INTRODUCTION

The early pre-occupation with compounds having sulphur donor atoms has given way to a much broader interest in the reactions of complexes containing not only sulphur donor atoms but also nitrogen and oxygen donor atoms. Many of these complexes have been found to be useful in metal chelation therapy¹, antiinfluenza, antiprotozoan, antibacterial and antiviral treatment². Recent researches are now geared towards the search for bio-active molecules especially in the area of biotechnology. New chemotherapeutic agents that can combat bacterial infections are of extreme importance now that antibiotic resistant strains of bacteria are an increasing threat to animal and human health³.

A number of workers have reported some transition metal coordination complexes containing C-S group^{2,4,5}. In these research works, the ligands and their metal complexes have been found to be potential source of chemotherapeutic agents. Comparatively less is known about the lanthanide metal coordination complexes containing C-S group. Lanthanides have an interesting but not well-known biological role in living organisms as trace elements⁶. Several reports by Kostova *et al.*⁷⁻¹⁰ have shown that the lanthanide(III) complexes of coumarins were potent cytotoxic and cytostatic agents.

In view of the noted cytotoxic activity of lanthanide(III) complexes and biological activity of thiolates, Ce(IV) and Nd(III) complexes of S-1,3-benzothiazol-2-ylthiophene-2-carbothioate (SBC) were synthesized, characterized and their antibacterial activities on *Escherichia coli*, *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* determined.

EXPERIMENTAL

All the reagents used were of analytical grade and were used as supplied unless otherwise stated. The electronic absorption spectra were recorded in ethanol on Unico-UV 2102 spectrophotometer. The conductivity measurements were carried out at room temperature in dimethyl sulphoxide using a dip type cell CD 600 model conductivity meter. The infrared spectra of the ligand and complexes were recorded in solution of carbon tetrachloromethane on a Puck Specific Model 500 IR spectrophotometer. The ^1H and ^{13}C NMR spectra of the ligand were recorded in CDCl_3 at room temperature on Varian Mercury-200BB NMR spectrophotometer, using tetramethylsilane as internal standard. The GC-MS of the ligand and complexes were recorded on GC-MS QP 2010 plus SHIMADZU, Japan Model.

Synthesis of S-1,3-benzothiazol-2-ylthiophene-2-carbothioate: The ligand was prepared by S-acylation of 2-mercaptobenzothiazole with thiophene-2-carbonylchloride in the presence of pyridine which acts as a catalyst¹¹. To a solution of 2-mercaptobenzothiazole (2.51 g, 0.015 mole), thiophene-2-carbonylchloride (1.60 mL, 0.015 mole) was added followed by 5 mL of pyridine. The mixture was heated with stirring over a water bath until fumes of hydrogen chloride ceased to appear. About 2 mL of distilled water was added, followed by 2 mL of pyridine to eliminate the excess reagent. The product solidified upon stirring with a glass rod into a white coloured solid. Water (10 mL) was added, the product filtered and recrystallized from dilute ethanoic acid. The yield was 40.38 % and the melting point 162 °C. The spectral results are as follows: UV (λ_{\max} nm, cm^{-1}) (ethanol): (256, 271, 336); (13, 845, 14,657, 18,172). IR (KBr, ν_{\max} , cm^{-1}): 3054 (s), 2985 (m), 1670 (m), 1560 (m), 1497 (m), 1420 (s), 1077 (s), 896 (s), 738 (sh), 706 (w). ¹H NMR (CDCl_3) (δ , ppm): 7.15 (1H, d), 7.20 (2H, t), 7.23 (1H, d), 7.25-7.40 (4H, m). ¹³C NMR (δ , ppm): 112.551, 121.412, 124.622, 127.232, 130.365, 141.002, 191.212.

Syntheses of Ce(IV) and Nd(III) complexes: The complexes were synthesized by refluxing ethanol solutions of $\text{Ce}(\text{SO}_4)_2$ and $\text{Nd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with the ligand, respectively in amounts equal to metal: ligand molar ratio of 1:2 to ensure complete reaction^{6,7}. To ethanolic solution (20 mL) of cerium(IV) sulphate (0.32 g, 0.004 mole) was added a solution of S-1,3-benzothiazol-2-ylthiophene-2-carbothioate (2.22 g, 0.008 mole) in ethanol (40 mL). The mixture was refluxed for 1 h under constant stirring at 80 °C. On cooling, milk coloured precipitate formed. They were filtered and dried in a desiccator over fused CaCl_2 . The yield was 62.82 %, melting point 170 °C and conductivity value of $127 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The spectral data are as follows: UV (λ_{\max} , nm, cm^{-1}) (ethanol): (219, 265, 316); (11, 844, 14, 332, 17, 090). IR (KBr, ν_{\max} , cm^{-1}): 3586 (br), 3053 (s), 2986 (s), 1664 (s), 1510 (m), 1418 (s), 1056 (m), 1060 (s), 895 (m), 808 (m), 738 (m), 485 (w).

The same procedure was repeated using neodymium(III) nitrate pentahydrate (1.69 g, 0.004 mole). A milk coloured precipitate was formed with yield of 42.37 %, melting point of 150 °C and conductivity value of $194 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The spectral data are as follows: UV (λ_{\max} , nm, cm^{-1}) (ethanol): (255, 284, 325); (13,791, 13,413, 17, 577). IR (KBr, ν_{\max} , cm^{-1}): 3596 (br), 3054 (s), 2987 (s), 1660 (s), 1515 (m), 1420 (s), 1352 (s), 1056 (m), 896 (m), 739 (sh), 482 (w).

Antibacterial studies: The inhibitory activity of the ligand and its metal complexes were carried out on some microorganisms which include: *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. The bacteria strains used were isolated from clinical conditions. *Escherichia coli* and *Pseudomonas aeruginosa* are Gram-negative rod while *Bacillus subtilis* and *Staphylococcus aureus* are Gram-positive. The method used was the agar well-diffusion technique¹².

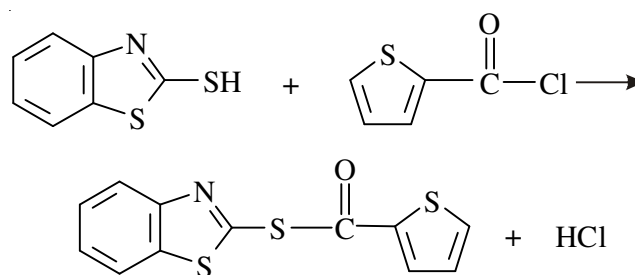
Mueller-Hinton agar plates were inoculated with 0.1 mL 3 h broth culture of the test microorganisms. Using a cork borer, wells (7 mm in diameter and 2.5 mm deep) were bored into the inoculated agar. A 20 mg/mL of the test extract was

prepared and 50 μL of each compound were delivered into the wells. One of the wells contained 20 % v/v DMSO while another two contained 20 mg/mL of ampicillin and tetracycline in DMSO, respectively. The plates were incubated at 37 °C for 24 h and assessment of antibacterial activity was based on the measurement of the diameter of inhibition zone (IZD) around the wells.

The minimum inhibitory concentrations (MIC) of the test compounds were determined using the agar well dilution method described by Ojo *et al.*¹³. Two-fold serial dilutions of test compound were made in 20 % v/v DMSO. One milliliter of each serial dilution was added to 19 mL of sterile Mueller-hinton agar maintained at 45 °C, thoroughly mixed and poured into a sterile plate and the medium allowed to solidify. The final concentration of the compounds ranged from 20 to 0.625 mg/mL. Inoculated plates were incubated at 37 °C for 24 h and observed for presence of visible growth. The minimum inhibition concentration was determined as the value of the lowest concentration that completely suppressed the growth of the microorganisms.

RESULTS AND DISCUSSION

The reaction of 2-mercaptobenzothiazole with thiophene-2-carbonylchloride yielded S-1,3-benzothiazol-2-ylthiophene-2-carbothioate (SBC) as shown in **Scheme-I**. The reaction of $\text{Ce}(\text{SO}_4)_2$ and $\text{Nd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with SBC yielded $[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$ and $[\text{Nd}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$, respectively. The ligand and complexes are air stable, powdery and non-hygroscopic with high melting points. S-1,3-benzothiazol-2-ylthiophene-2-carbothioate and its metal complexes were soluble in DMSO and methanol but insoluble in water. Jobs continuous variation gave a 1:2 metal to ligand stoichiometry for both complexes.



Scheme-I: Synthesis of ligand

Conductivity measurements: The observed molar conductance of 10^{-3}M in DMSO solution at room temperature for the metal complexes, indicate that they are electrolytes. The values of the conductivities (127.00 and $194.00 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) approach those expected for 1:2 and 1:3 complexes, respectively¹⁴.

Electronic absorption spectra: S-1,3-Benzothiazol-2-ylthiophene-2-carbothioate show strong absorption at 256, 271 and 336 nm. These have been assigned to $n-\pi^*$ and $\pi-\pi^*$ transitions within the ligand¹⁵. The existence of many $n-\pi^*$ transition in SBC indicate the presence of elements with non-bonding electrons on the compound. In $[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$, blue shifts were observed from λ_{\max} of 256 nm, 271, 336 nm in

SBC to 219, 265 and 316 nm in $[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$. This is as a result of the ligand bonding to the metal through the non-bonding electrons^{15,16}. In both complexes, the observed peaks were below $25,000\text{ cm}^{-1}$ suggesting that there were no charge transfer transition¹⁷.

Infrared spectra: The IR spectra of SBC showed the absence of band around $2600\text{--}2550$ and $1800\text{--}1770\text{ cm}^{-1}$ due to $\nu(\text{S-H})$ and $\nu(\text{COCl})$ stretching vibrations and a strong new band appeared at 1077 cm^{-1} assigned to thiocarbonyl group¹⁸. This confirms the formation of the ligand from 2-mercapto-benzothiazole and thiophene-2-carbonyl chloride. Presence of broad bands around $3596\text{--}3586\text{ cm}^{-1}$ in the IR spectra of the metal complexes indicate that water is coordinated to the metal ions¹⁹. The bands between $3054\text{--}2985\text{ cm}^{-1}$ in the spectra of the ligand and metal complexes were assigned to C-H stretching vibrations. A medium band assigned to $\nu(\text{C=O})$ stretch of the carboxylic group was observed around 1670 cm^{-1} in the ligand but was observed as a strong band around 1664 and 1660 cm^{-1} in $[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$ and $[\text{Nd}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$, respectively. This band shifted to lower frequencies in the metal complexes indicating that the ligand binds to the metal ions through the oxygen atom of the carbonyl group. The medium bands in the $1560\text{--}1497\text{ cm}^{-1}$ region in the ligand and complexes were assigned to $\nu(\text{C=N})$ of the benzothiazole ring. Similar observation has been made in literature^{20,21}. This band shifted to lower frequencies of about 50 cm^{-1} in the metal complexes, suggesting coordination through the C=N of the benzothiazole ring. This is further supported by the emergence of bands around $485\text{--}482\text{ cm}^{-1}$ in the metal complexes assigned to M-N^{22,23}. The bands at 1077 , 1056 and 1056 cm^{-1} in the ligand, $[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$ and $[\text{Nd}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$, respectively were assigned to the thiocarbonyl group¹⁹. This band shifted to lower values in both complexes indicating that complexation occurred in this group. Coordination of the metal ions to the ligand through the sulphur atom of the thiocarbonyl group was ruled off since the $\nu(\text{C-S})$ remained relatively the same in the compounds. On the other hand, the spectra of the complexes showed new bands at 1352 and 1060 cm^{-1} ascribed to vibrations of ionic nitrate^{24,25} and ionic sulphate²⁶, respectively.

Nuclear magnetic resonance: S-1,3-benzothiazol-2-ylthiophene-2-carbothioate showed a doublet peak at 7.15 ppm, triplet peak at 7.20 ppm and doublet peak at 7.23 ppm. All these were attributed to thiophene protons. The chemical shifts obtained in the range $7.25\text{--}7.40$ ppm were assigned to benzothiazole protons.

The ^{13}C NMR for the ligand gave signal at 112.551 and 121.412 ppm, attributed to methine carbons (8, 9 and 10) (Fig. 1) on thiophene ring while the signals at 124.622 and 127.232 ppm were attributed to methine carbons (1 and 2) on the phenyl ring. The signal at 141.002 ppm was assigned to quaternary carbon (5) because it is attached to three electronegative groups hence it is more deshielded than the other quaternary carbons attached to only one electronegative group. The carbonyl carbon (6) was observed at 191.212 ppm. This value is so assigned because the carbonyl carbon is the most deshielded due to the influence of the electronegative elements and the benzothiazole ring. It was also recognized by its low intensity²⁷.

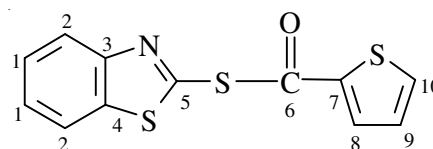
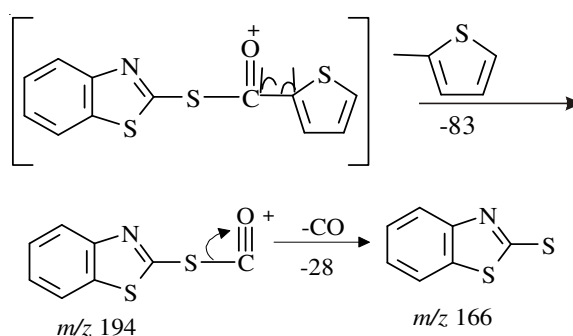


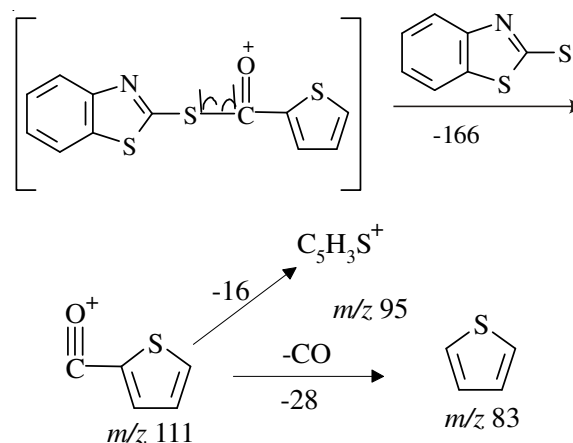
Fig. 1. Structure of the ligand showing carbon numbering

Gas chromatography-mass spectroscopy: The chromatogram of SBC gave eight components. Component 3 is the most prominent and its mass spectrum gave a base peak of m/z 167. A careful study of mass spectrum of the various components show that the relevant components are 3 and 5. The molecular ion, M^+ of component 3 is evident with m/z 167 and $M^+ + 2 = 169$. The (M^+) for component 5 has m/z 111 with $M^+ + 1 = 122$. The peaks with m/z 167 and 111 may have arisen as a result of the possible fragmentation of the compound as shown in Schemes II and III.



Scheme-II: Fragmentation pattern of S-1,3-benzothiazol-2-ylthiophene-2-carbothioate through thiophene ring

Based on this, the molecular weight of SBC = 278 g. This is close to the calculated value of 277 g. The chromatogram of Ce(IV) complex of SBC gave eight components. From the mass spectrum, components 1-8 have base peaks of m/z 55, 167, 73, 195, 181, 83, 55 and 111, respectively. Based on this, molecular weight of $[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2 = 920$ g, calculated value = 922 g.



Scheme-III: Fragmentation pattern of S-1,3-benzothiazol-2-ylthiophene-2-carbothioate through benzothiazole ring

The chromatogram of Nd(III) complex of SBC gave 10 components. From the mass spectrum, the relevant components are components 1, 2, 4, 6-10 with base peaks of m/z 55, 167,

73, 83, 181, 195, 55 and 111. Based on this the molecular weight of $[\text{Nd}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3 = 920 \text{ g}$, calculated value = 920 g.

Antibacterial activity: The inhibitory activity of SBC and its Ce(IV) and Nd(III) complexes were tested on some microorganisms which include: *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. The result is presented in Table-1 while the minimum inhibition concentration (MIC) on each of the microorganism is shown in Table-2.

TABLE-1
ANTIBACTERIAL ACTIVITY OF SBC
AND ITS Ce(IV) AND Nd(III) COMPLEXES

Compound (20 mg/mL)	<i>B. subtilis</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>
SBC	20	15	12	-
$[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$	11	10	-	-
$[\text{Nd}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$	13	11	-	-
Ampiciline	24	22	17	18
Tetracycline	18	17	21	20

TABLE-2
MINIMUM INHIBITION CONCENTRATION

Ligand/complexes	Zone of inhibition (mm) organism: <i>Bacillus subtilis</i>				
	10 mg/mL	5 mg/mL	2.5 mg/mL	1.25 mg/mL	0.625 mg/mL
SBC	18	16	14	12	-
$[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$	10	10	10	-	-
$[\text{Nd}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$	11	11	10	-	-
Organism: <i>Staphylococcus aureus</i>					
SBC	13	10	10	-	-
$[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$	-	-	-	-	-
$[\text{Nd}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$	-	-	-	-	-
Organism: <i>Escherichia coli</i>					
SBC	-	-	-	-	-
$[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$	-	-	-	-	-
$[\text{Nd}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$	-	-	-	-	-
Organism: <i>Pseudomonas aeruginosa</i>					
SBC	-	-	-	-	-
$[\text{Ce}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{SO}_4)_2$	-	-	-	-	-
$[\text{Nd}(\text{SBC})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$	-	-	-	-	-

From the result obtained, SBC has shown to be active against *Bacillus subtilis*, *Staphylococcus aureus* and *Escherichia coli* while its Ce(IV) and Nd(III) complex were active against the Gram-positive bacteria *Bacillus subtilis* and *Staphylococcus aureus* but showed no activity on the Gram-negative bacteria, *Escherichia coli* and *Pseudomonas aeruginosa*. SBC showed a higher antibacterial activity against *Bacillus subtilis* than does tetracycline, which was used as a standard.

Conclusion

S-1,3-Benzothiazol-2-ylthiophene-2-carbonylchloride, and its Ce(IV) and Nd(III) complexes were successfully synthesized and characterized. This resulted in the formation of octahedral complexes. The possible structures of the complexes are shown in Fig. 2. S-1,3-Benzothiazol-2-ylthiophene-2-carbonylchloride and its Ce(IV) and Nd(III) complexes have shown to be active against Gram-positive bacteria (*Bacillus*

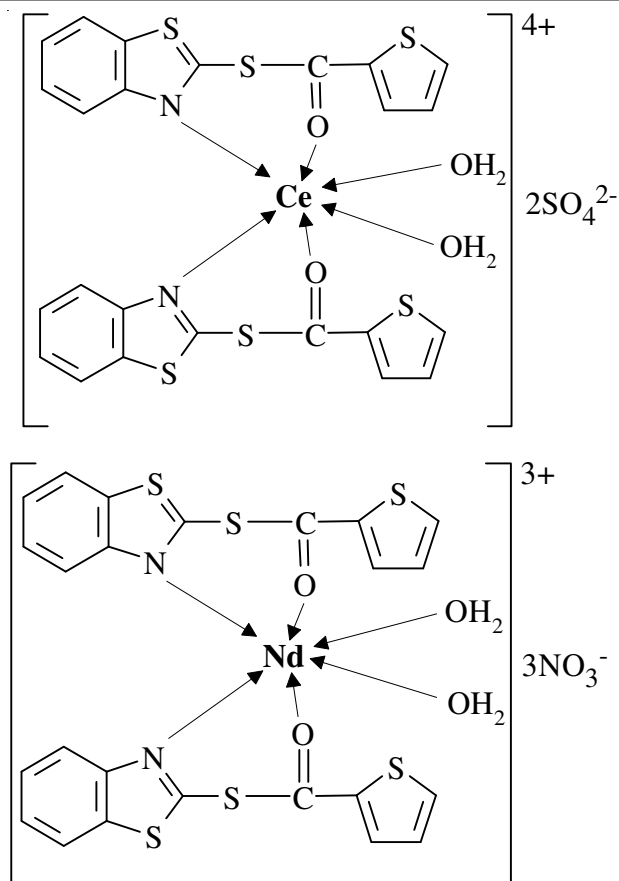


Fig. 2. Proposed structure of Ce(IV) and Nd(III) complexes

subtilis and *Staphylococcus aureus*) than Gram-negative bacteria. Hence, they could be used as antibacterial drugs.

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