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Synthetic aspects, spectral, thermal studies and antimicrobial screening on *bis*(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)antimony(III) complexes with oxo or thio donor ligands

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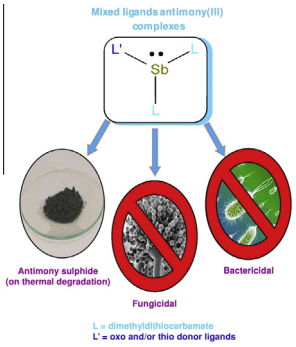
HIGHLIGHTS

- Mixed *bis*(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)antimony(III) complexes.
- The complexes adopted distorted octahedral geometry with lone pair of electrons.
- These are crystalline in nature, nano-ranged and having monoclinic crystal system.
- Antimony sulfide was a final decomposition product upon thermal decomposition.
- These showed a greater or equal antimicrobial activity than the standard drugs.

GRAPHICAL ABSTRACT



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ABSTRACT

The *bis*(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)antimony(III) complexes have been obtained by the reaction of chloro *bis*(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)antimony(III) with corresponding oxo or thio donor ligands such as sodium benzoate **1**, sodium thioglycolate **2**, phenol **3**, sodium 1-propanethiolate **4**, potassium thioacetate **5**, sodium salicylate **6**, ethane-1,2-dithiolate **7** and disodium oxalate **8**. These complexes have been characterized by the physicochemical [melting point, molecular weight determination and elemental analysis (C, H, N, S and Sb)], spectral [UV–Visible, FT-IR, far IR, NMR (^{1}H and ^{13}C)], thermogravimetric (TG & DTA) analysis, ESI-Mass and powder X-ray diffraction studies. Thermogravimetric analysis of the complexes confirmed the final decomposition product as highly pure antimony sulfide (Sb_2S_3) and powder X-ray diffraction studies show that the complexes are in lower symmetry with monoclinic crystal lattice and nano-ranged particle size (11.51–20.82 nm). The complexes have also been screened against some bacterial and fungal strains for their antibacterial and antifungal activities and compared with standard drugs. These show that the complexes have greater activities against some human pathogenic bacteria and fungi than the activities of standard drugs.

Introduction

Dithiocarbamates owe special significance due to their wide spread applications such as vulcanization additives, stabilizers for PVC, nitrogen–oxygen trapping agents, chelating agents of heavy

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metals, lubricants and catalysts [1–4]. They have also been used as biologically active molecules [4,5–9] such as fungicides, bactericides, anticancer agents [10–12] and as arrestors of human immunodeficiency virus (HIV) infections such as AIDS [13–15]. The antimicrobial effect of dithiocarbamates has been reported to arise by the reaction of HS-groups with physiologically important enzymes by transferring the alkyl group of the dithioester to the HS-function of the enzyme [19,20].

These are versatile ligands with remarkable diversities in their bonding and coordination pattern with main group metals [16–21] and have been widely studied [1–4,5–9]. A number of metal dithiocarbamate complexes have been used in analytical chemistry [22], as antioxidants [23,24], polymer photo stabilizers [25] and precursor for creating sulfide film semiconductors [26]. Trivalent antimony compounds have also been used as drugs for the treatment of laishmaniasis span more than 50 years [27,28]. Antimony metal complexes containing Sb—S bonds have been widely used in industrial processes [29] as well as antimony derivatives of carboxylic and phenolic ligands have also been used as antiwear agents or multifunctional additive to lubricants [30]. Thermal degradation of such type of complexes yield highly pure binary antimony sulfide (Sb_2S_3) as final degradation product, which is a kind of semiconductor with its interesting high thermoelectric power. It is a layer-structured direct band gap semiconductor with orthorhombic crystal structure [31] and considered a promising material for solar energy owing to its band gap that covers the range of the solar spectrum [32]. It has been extensively investigated for its special applications as a target material for microwave devices [33], television cameras, switching devices [34], rechargeable storage cells [35] and various optoelectronic devices [36].

In view of the wide range of applications and to keep forward the our research on the design, characterization and development of new biologically active agents containing group 15 metals [37–41], we have synthesized new mixed antimony(III) dimethyldithiocarbamato complexes with oxo or thio donor ligands and characterized by a variety of analytical techniques: physicochemical [melting point, molecular weight determination and elemental analysis (C, H, N, S and Sb)], spectral [UV–Visible, FTIR, far IR, NMR (^{1}H and ^{13}C)], thermal (TGA, DTA and ESI-Mass) analysis and powder X-ray diffraction studies. The free ligands and their antimony complexes have also been screened for their bactericidal and fungicidal effects. These exhibit higher bactericidal and fungicidal effect in comparison to free ligands and some standard antibiotics used.

Experimental

Material and methods

The precursors and complexes form are highly moisture sensitive; therefore, all the experimental manipulations have been carried out under moisture free conditions. Antimony(III) chloride (E. Merck) was purified by distillation before use. Sodium dimethyldithiocarbamate (Aldrich) and ligands [sodium benzoate, sodium thioglycolate, phenol, sodium 1-propanethiolate, potassium thioacetate, sodium salicylate, ethane-1,2-dithiol and disodium oxalate (all Aldrich and E. Merck)] were used as received without further purification. Solvent (hexane, dichloromethane, chloroform, acetonitrile, etc.) were purified by standard methods [42]. *Tris*(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)antimony(III) and chloro*bis*(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)antimony(III) were prepared by the method reported in the literature [40,43].

Synthesis of new complexes

*Synthesis of compound **1**–**6** in 1:1 M ratios*

Chloro*bis*(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)antimony(III) (1.9 g; 4.8 mmol) dissolved in hexane (~40 ml) was added to sodium benzoate **1** (0.7 g; 4.8 mmol) drop-wise. The reaction mixture was refluxed for ~5 h. It was then cooled and precipitated sodium salt was filtered off. The filtrate was reduced under vacuum to obtain the product (Scheme 1).

Compounds (**2**–**6**) were also synthesized by adopting the similar procedure.

*Synthesis of compound **7** and **8** in 2:1 M ratios*

The hexane solution (~40 ml) of chloro*bis*(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)antimony(III) (2.6 g; 6.6 mmol) was added dropwise to hexane solution of ethane-1,2-dithiol **7** (0.3 g; 3.3 mmol). The reaction mixture was refluxed for ~5 h followed by filtration. The product was obtained by reducing the solvent under vacuum. The compound **8** have also been prepared by similar procedure. All pertinent analytical and physicochemical data have been summarized in Table 1.

Antimicrobial evaluation

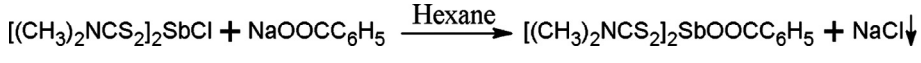
Test micro-organism strains

The ligands used and their synthesized complexes were screened *in vitro* for their antimicrobial activities against four human pathogenic bacterial species [*Staphylococcus aureus* (ATCC 9144) (G^{+ve}), *Bacillus subtilis* (ATCC 6051) (G^{+ve}), *Escherichia coli* (ATCC 9637) (G^{-ve}) and *Pseudomonas aeruginosa* (ATCC 25619) (G^{-ve})] and two plant fungal species [*Aspergillus niger* (ATCC 9029) and *Trichoderma ressie* (ATCC 164)] by using the well diffusion method [37,44]. Standard drugs such as chloramphenicol and terbinafine were used as a reference for antibacterial and antifungal screening respectively.

Method

The compound was dissolved in DMF, to get 200 μg mL^{-1} solution. Further progressive double dilutions were performed to obtain the required concentrations of 100 and 50 μg mL^{-1}. A 0.5 mL solution of the each investigated micro-organisms was added to a sterile nutrient agar (for bacteria)/dextrose agar (for fungi) medium just before solidification, then poured onto sterile Petri dishes (9 cm in diameter) and left to solidify. Using sterile cork borer (6 mm in diameter), three holes (wells) were made in each dish and then 0.1 mL of tested compound dissolved in DMF (50, 100 and 200 μg mL^{-1}) was poured into these holes. Finally the dishes were incubated at 37 °C (24 h) for bacteria and at 30 °C (72 h) for fungi, where clear or inhibition zones were detected around each hole (Fig. S1a and b). Inhibitory activities were measured (in mm) as diameter of the inhibition zones.

A quantity of 0.1 ml DMF alone was used as a control under the same conditions for each organism and by subtracting the diameter of inhibition zone resulting with DMF from that obtained in each case, both antibacterial and antifungal activities can be calculated as a mean of three replicates.



Scheme 1. Synthetic route of compound **1**.