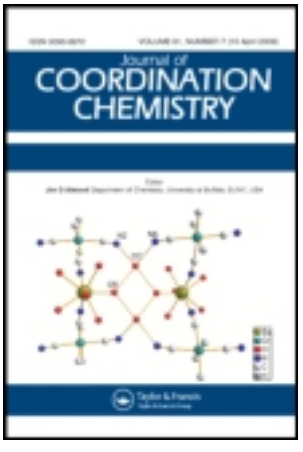

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, structural and thermal studies of some biologically active antimony semicarbazones and thiosemicarbazones

Narayan V. Sawant [a], Jasmine B. Biswal [a] & Shivram S. Garje [a]
[a] Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (East), Mumbai 400 098, Maharashtra, India
Published online: 19 May 2011.

To cite this article: Narayan V. Sawant, Jasmine B. Biswal & Shivram S. Garje (2011) Synthesis, structural and thermal studies of some biologically active antimony semicarbazones and thiosemicarbazones, Journal of Coordination Chemistry, 64:10, 1758-1769, DOI: 10.1080/00958972.2011.572163

To link to this article: http://dx.doi.org/10.1080/00958972.2011.572163

Journal of Coordination Chemistry
Vol. 64, No. 10, 20 May 2011, 1758–1769

Taylor & Francis
Taylor & Francis Group

Synthesis, structural and thermal studies of some biologically active antimony semicarbazones and thiosemicarbazones

NARAYAN V. SAWANT, JASMINE B. BISWAL and SHIVRAM S. GARJE*

Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (East), Mumbai 400 098, Maharashtra, India

(*Received 6 March 2010; in final form 23 February 2011*)

The reactions of Ph_3SbCl_2 and $SbCl_3$ with semicarbazone and thiosemicarbazone ligands resulted in $Ph_3SbCl_2(L)$ and $SbCl_3(L)$ (L = semicarbazone and thiosemicarbazone ligands). These complexes were characterized by elemental analyses, IR, ^1H and $^{13}C\{^1H\}$ NMR spectral data, and conductometric measurements. On the basis of spectroscopic data, a seven-coordinate and a five-coordinate antimony with ligand coordination through oxygen/sulfur and azomethine nitrogen have been suggested for $Ph_3SbCl_2(L)$ and $SbCl_3(L)$, respectively. These compounds show antifungal and antibacterial activities. Thermal behavior of some of the adducts have been studied by thermogravimetric analyses. Thermal decomposition of $Ph_3SbCl_2(L)$ and $SbCl_3(L)$ resulted in micron size Sb and Sb_2S_3 particles. The materials obtained were characterized by powder X-ray diffraction patterns, scanning electron microscopy, and energy dispersive X-ray analysis (EDAX).

Keywords: Antimony complexes; Antimony sulfide; Semicarbazone; Thiosemicarbazone; Antifungal; Antibacterial

1. Introduction

The coordination chemistry [1], analytical applications [2, 3], and biological activities (antibacterial, antimalarial, antiviral, and fungicidal) [1, 4–6] of semicarbazone and thiosemicarbazone complexes have been studied. Semicarbazones and thiosemicarbazones are monodentate, bidentate, or multidentate chelating ligands for metal ions based on the type of aldehyde or ketone used for condensation [3]. Some of these ligands show biological activity; thiosemicarbazones have biological activity against viruses, protozoas, pathogens, and some types of tumors [7]. West *et al*. [8] reported that the coordination of thiosemicarbazones with transition metal ions, such as copper(II), nickel(II) etc., often increases their biological activities. An increase in biological activity of thiosemicarbazones after chelation has been reported by many other workers [9–12]. For example, antibacterial activities of bismuth(III) complexes of some thiosemicarbazones are reported to be superior to the free ligand [10]. This increase in activity has been attributed to reduced polarity of metal after complexation/chelation. In complexes, there is delocalization of positive charge of the metal with the

*Corresponding author. Email: ssgarje@chem.mu.ac.in

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2011.572163

donor groups and in chelates, possibly there is π-electron delocalization within the whole ring. This increases the hydrophobic character which enhances penetration through lipoid layers of microorganism causing their death [13]. Semi- and thiosemicarbazones are versatile molecules coordinating either as a neutral ligand or as a charged/deprotonated ligand through O, N, N– or S, N, N– [14]. Though many transition metal complexes [6, 13, 15–21] containing these ligands are reported, only a few reports are available on their antimony complexes [22–26].

Attention has been directed toward the investigation of single-source precursors for semiconductor materials. Group V-chalcogenide materials have been widely studied as they possess good photoconductivity, photosensitivity, IR spectroscopic, and high thermoelectric properties [27–30]. Antimony is a semi-metal with an energy overlap of 180 mV between the conduction and valence bands at 4.2 K [31]. Owing to its unique physical properties such as low carrier densities, long Fermi wavelength, and high carrier mobilities, it is valuable in both fundamental research and practical applications. For instance, the III–V Sb-based semiconductors play an important role in electronics, optoelectronics, and thermoelectric materials [32]. Antimony sulfide (Sb_2S_3), a member of group V–VI binary metal chalcogenides, belongs to the family of solid-state materials with potential applications in thermoelectric cooling technologies [33], television cameras [34], microwave devices [35], optoelectronic devices [36], switching devices [37], and write-once read-many times (WORM) kind of storage applications [38]. Due to its good photoconductivity, Sb_2S_3 is regarded as a promising material for solar energy [39] as its band gap (1.78–2.5 eV) covers the range of the solar energy spectrum [40].

Recently, we reported the deposition of Sb_2S_3 thin films using $SbCl_3$(thiosemicarbazone) complexes as single source precursors [41]. We thought it worthwhile to study the synthesis, characterization, antifungal, and antibacterial activities of antimony(V) and (III) semicarbazone and thiosemicarbazone complexes and to explore their suitability as single-source precursors for semiconductor materials.

2. Experimental

Analytical grade solvents were used; they were dried prior to use. Triphenylantimony(V)dichloride was prepared by chlorination of triphenylantimony (Lancaster) in carbon tetrachloride. Antimony(III)chloride (S.D. fine) was used after vacuum distillation (73°C/1–2 mm of Hg). The ligands were prepared by the reported methods [3, 42, 43]. Reactions involving antimony(III)chloride were carried out in an oxygen-free nitrogen atmosphere as it is sensitive to moisture. However, the resulting complexes are air stable. The elemental analysis was carried out in the microanalytical laboratory of this department. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrophotometer using KBr pellets from 4000 to 400 cm^{-1}. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in DMSO-d_6 on a Bruker Avance II 300 MHz NMR spectrometer. The chemical shifts are relative to internal standard tetramethylsilane. Conductometric measurements were carried out in dry DMF on a Toshniwal conductometer. The melting points taken are uncorrected. Thermogravimetric analysis (TGA) was carried out on a Pyris Diamond TG/DTA Perkin-Elmer instrument at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. XRD patterns of the materials were recorded using Cu-Kα radiation on a Philips X'pert PRO PANalytical X-ray

diffractometer with an accelerating voltage of 45 kV at a scanning rate of $0.05^\circ\ s^{-1}$. JEOL JSM-840 scanning electron microscope (SEM) with an accelerating voltage of 20 kV was used to observe the morphologies of the materials. Compositional analysis of the materials obtained was carried out on EDAX (Inca Energy, model of Oxford).

2.1. *Synthesis*

Ph_3SbCl_2(L) and $SbCl_3$(L) (where L = semicarbazone of pyridine-2-carboxaldehyde (pyscz), furfuraldehyde (furscz), thiophene-2-carboxaldehyde (thiopscz), salicylaldehyde (salscz), *trans*-cinnamaldehyde (cinnamscz), *trans*-2-nitrocinnamaldehyde (*trans*-2-NO_2-cinnamscz), indole-3-carboxaldehyde (ind-3-carbscz), 4-chlorobenzaldehyde (4-Cl-benzscz), 4-fluoroacetophenone (4-F-acphscz), acetone (acscz), and methylisopropylketone (mipkscz); and thiosemicarbazones of *trans*-cinnamaldehyde (cinnamtscz), *trans*-2-nitrocinnamaldehyde (*trans*-2-NO_2-cinnamtscz), and 4-fluoroacetophenone (4-F-acphtscz)] were prepared; preparations of representative complexes are given below.

2.1.1. Synthesis of Ph_3SbCl_2(4-F-acphscz). Around 0.435 g (2.23 mmol) of 4-fluoroacetophenone semicarbazone in 30 mL dry THF was added dropwise into 0.944 g (2.23 mmol) of triphenylantimony(V)dichloride with constant stirring and the stirring was continued for 12 h. Then the solvent was evaporated under vacuum and the resulting solid washed repeatedly with cyclohexane (5×10 mL). The product was recrystallized from THF and hexane mixture, dried *in vacuo* and weighed (yield 0.515 g, 37.37%), m.p. 178°C, Anal. Calcd for $SbCl_2C_{27}H_{25}N_3OF$ (%): Sb, 19.66; Cl, 11.45; C, 50.43; H, 3.58; N, 6.78. Found (%): Sb, 19.32; Cl, 11.66; C, 50.20; H, 3.14; N, 7.35. IR: 3443 cm^{-1} ν_{NH2} asym, 3308 cm^{-1} ν_{NH2} sym, 3050 cm^{-1} ν_{NH}, 1740 cm^{-1} $\nu_{C=O}$, 1580 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 2.1 (s, CH_3), 6.5 (s, NH_2), 7.1–8.1 (m, $Ph_3Sb + C_6H_4$), 9.3 (s, NH). ^{13}C NMR: Ph_3Sb: 143.83 (C-i), 133.92 (C-o), 132.23 (C-p), 130.25 (C-m); ligand moiety: 157.81 (>C=O), 135.16 (>C=N), 128.63, 128.52, 115.56, 115.27 (C_6H_4), 13.73 (CH_3). TGA: calculated weight loss for the formation of Sb (Calcd 80.34%, Obs. 79.96%).

2.1.2. Synthesis of $SbCl_3$(4-F-acphtscz). To a weighed quantity of 4-fluoroacetophenone thiosemicarbazone (0.463 g, 2.19 mmol) in 30 mL dry THF, 0.500 g (2.19 mmol) of antimony(III)chloride in 10 mL dry THF was added under nitrogen and the solution stirred for 13 h at room temperature. The solvent was evaporated under reduced pressure to give a white solid which was repeatedly washed with cyclohexane (5×10 mL). Then it was recrystallized from THF and hexane mixture, dried *in vacuo*, and weighed (yield 0.862 g, 89.53%), m.p. 162°C, Anal. Calcd for $SbCl_3C_9H_{10}N_3SF$ (%): Sb, 27.71; Cl, 24.20; C, 24.60; H, 2.29; N, 9.56. Found (%): Sb, 27.71; Cl, 23.89; C, 25.04; H, 2.72; N, 9.35. IR: 3450 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3180 cm^{-1} ν_{NH}, 810 cm^{-1} $\nu_{C=S}$, 1595 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 2.2 (s, CH_3), 7.1–8.2 (m, $NH_2 + C_6H_4$), 10.1 (s, NH). ^{13}C NMR: 179.00 (>C=S), 147.58 (>C=N), 134.57, 129.39, 115.87, 115.14 (C_6H_4), 14.6 (CH_3). TGA: calculated weight loss for the formation of Sb_2S_3 (Calcd 61.34%, Obs. 68.00%).

Similarly, all other complexes were prepared. The physical and analytical data of these complexes are given below.

2.1.3. Ph_3SbCl_2(pyscz). Yield 0.610 g (77.60%), m.p. 156°C, Anal. Calcd for $SbCl_2C_{25}H_{23}N_4O$ (%): Sb, 20.70; Cl, 12.05; C, 51.05; H, 3.94; N, 9.52. Found (%): Sb, 20.52; Cl, 11.64; C, 51.25; H, 3.45; N, 9.04. IR: 3400 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3100 cm^{-1} ν_{NH}, 1670 cm^{-1} $\nu_{C=O}$, 1580 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.2 (s, NH_2), 6.6–8.4 (m, $Ph_3Sb + C_5H_4N + CH$), 10.2 (s, NH). ^{13}C NMR: Ph_3Sb: 142.21 (C-i), 133.97 (C-o), 132.12 (C-p), 130.17 (C-m); ligand moiety: 156.91 (>C=O), 153.88 (>C=N), 149.20, 139.68, 137.34, 124.01, 120.29 (C_5H_4N).

2.1.4. Ph_3SbCl_2(furscz). Yield 0.272 g (52.81%), m.p. 168°C, Anal. Calcd for $SbCl_2C_{24}H_{22}N_3O_2$ (%): Sb, 21.09; Cl, 12.28; C, 49.95; H, 3.66; N, 7.28. Found (%): Sb, 21.10; Cl, 12.56; C, 49.58; H, 3.24; N, 6.95. IR: 3450 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3060 cm^{-1} ν_{NH}, 1660 cm^{-1} $\nu_{C=O}$, 1600 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.3 (s, NH_2), 6.5–8.1 (m, $Ph_3Sb + C_4H_3O + CH$), 10.2 (s, NH). ^{13}C NMR: Ph_3Sb: 142.12 (C-i), 133.97 (C-o), 132.14 (C-p), 130.19 (C-m); ligand moiety: 156.98 (>C=O), 150.32 (>C=N), 144.47, 130.45, 112.41, 111.40 (C_4H_3O).

2.1.5. Ph_3SbCl_2(thiopscz). Yield 0.380 g (53.07%), m.p. 194°C, Anal. Calcd for $SbCl_2C_{24}H_{22}N_3SO$ (%): Sb, 20.52; Cl, 11.95; C, 48.59; H, 3.73; N, 7.08. Found (%): Sb, 20.32; Cl, 11.91; C, 48.48; H, 3.38; N, 6.86. IR: 3450 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3070 cm^{-1} ν_{NH}, 1650 cm^{-1} $\nu_{C=O}$, 1600 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.2 (s, NH_2), 7.0–8.1 (m, $Ph_3Sb + C_4H_3S + CH$), 10.2 (s, NH). ^{13}C NMR: Ph_3Sb: 142.18 (C-i), 133.96 (C-o), 132.14 (C-p), 130.19 (C-m); ligand moiety: 156.81 (>C=O), 139.87 (>C=N), 135.32, 129.23, 127.87, 114.59 (C_4H_3S).

2.1.6. Ph_3SbCl_2(salscz). Yield 0.205 g (31.63%), m.p. 212°C, Anal. Calcd for $SbCl_2C_{26}H_{24}N_3O_2$ (%): Sb, 20.18; Cl, 11.75; C, 51.77; H, 4.01; N, 6.96. Found (%): Sb, 20.37; Cl, 12.02; C, 51.28; H, 3.82; N, 6.64. IR: 3500 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3050 cm^{-1} ν_{NH}, 1680 cm^{-1} $\nu_{C=O}$, 1590 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.6–8.1 (m, $NH_2 + Ph_3Sb + C_6H_4 + CH$), 10.0 (s, NH), 10.2 (s, OH). ^{13}C NMR: Ph_3Sb: 141.78 (C-i), 133.51 (C-o), 131.66 (C-p), 130.18 (C-m); ligand moiety: 156.66 (>C=O), 155.78 (>C=N), 137.41, 129.71, 126.63, 120.58, 119.21, 115.93 (C_6H_4).

2.1.7. Ph_3SbCl_2(cinnamscz). Yield 0.340 g (54.57%), m.p. 192°C, Anal. Calcd for $SbCl_2C_{28}H_{26}N_3O$ (%): Sb, 19.86; Cl, 11.56; C, 54.85; H, 4.27; N, 6.85. Found (%): Sb, 19.81; Cl, 11.25; C, 54.84; H, 3.92; N, 6.48. IR: 3450 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3050 cm^{-1} ν_{NH}, 1640 cm^{-1} $\nu_{C=O}$, 1600 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.9–8.2 (m, $NH_2 + Ph_3Sb + C_6H_5 + CH{=}N + \underline{CH}{=}CH$–), 9.9 (s, NH). ^{13}C NMR: Ph_3Sb: 142.19 (C-i), 133.97 (C-o), 132.12 (C-p), 130.17 (C-m); ligand moiety: 156.96 (>C=O), 142.32 (>C=N), 136.63, 136.59, 129.26, 128.83, 127.12, 126.11 (C_6H_5).

2.1.8. Ph_3SbCl_2(*trans*-2-NO_2-cinnamscz). Yield 0.570 g (72.15%), m.p. 195°C, Anal. Calcd for $SbCl_2C_{28}H_{25}N_4O_3$ (%): Sb, 18.49; Cl, 10.77; C, 51.10; H, 3.81; N, 8.48.

Found (%): Sb, 18.66; Cl, 10.50; C, 50.80; H, 3.56; N, 8.14. IR: 3450 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3050 cm^{-1} ν_{NH}, 1670 cm^{-1} $\nu_{C=O}$, 1575 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.3 (s, NH_2), 6.9–8.2 (m, $Ph_3Sb + C_6H_4 + \underline{CH}{=}CH$), 10.3 (s, NH). ^{13}C NMR: Ph_3Sb: 142.03 (C-i), 133.91 (C-o), 131.95 (C-p), 130.05 (C-m); ligand moiety: 156.69 (>C=O), 148.02 (>C=N), 141.30, 131.07, 129.46, 128.88, 128.29, 124.84 (C_6H_4).

2.1.9. Ph_3SbCl_2(ind-3-carbscz). Yield 0.225 g (50.90%), m.p. 185°C, Anal. Calcd for $SbCl_2C_{28}H_{24}N_4O$ (%): Sb, 19.44; Cl, 11.32; C, 53.70; H, 3.86; N, 8.94. Found (%): Sb, 18.99; Cl, 11.06; C, 53.24; H, 3.44; N, 8.45. IR: 3400 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3050 cm^{-1} ν_{NH}, 1670 cm^{-1} $\nu_{C=O}$, 1570 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.2 (s, NH_2), 7.1–8.2 (m, br, $Ph_3Sb + C_8H_6N + CH$), 9.8 (s, NH). ^{13}C NMR: Ph_3Sb: 141.00 (C-i), 133.95 (C-o), 132.16 (C-p), 130.20 (C-m); ligand moiety: 157.39 (>C=O), 138.05 (>C=N), 137.41, 129.45, 124.49, 122.83, 122.21, 120.71, 112.11 (C_8H_6N).

2.1.10. Ph_3SbCl_2(4-Cl-benzscz). Yield 0.156 g (32.50%), m.p. 210°C, Anal. Calcd for $SbCl_3C_{26}H_{23}N_3O$ (%): Sb, 19.58; Cl, 17.11; C, 50.23; H, 3.72; N, 6.76. Found (%): Sb, 19.30; Cl, 17.37; C, 50.72; H, 3.68; N, 7.26. IR: 3450 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, ~3050 cm^{-1} ν_{NH}, 1670 cm^{-1} $\nu_{C=O}$, 1590 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.4–8.2 (m, $NH_2 + Ph_3Sb + C_6H_4 + CH$), 10.2 (s, NH). ^{13}C NMR: Ph_3Sb: 141.00 (C-i), 133.94 (C-o), 132.18 (C-p), 130.22 (C-m); ligand moiety: 157.17 (>C=O), 138.51 (>C=N), 134.18, 133.84, 129.06, 128.64 (C_6H_4).

2.1.11. Ph_3SbCl_2(acscz). Yield 0.459 g (72.28%), m.p. 140°C, Anal. Calcd for $SbCl_2C_{22}H_{24}N_3O$ (%): Sb, 22.58; Cl, 13.15; C, 49.01; H, 4.42; N, 7.79. Found (%): Sb, 22.46; Cl, 12.99; C, 49.14; H, 4.24; N, 7.44. IR: 3480 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3080 cm^{-1} ν_{NH}, 1680 cm^{-1} $\nu_{C=O}$, 1580 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 1.8 (d, 7 Hz, $C(CH_3)_2$), 6.1 (s, br, NH_2), 7.0–8.2 (m, Ph_3Sb), 8.9 (s, NH). ^{13}C NMR: Ph_3Sb: 142.27 (C-i), 133.97 (C-o), 132.11 (C-p), 130.16 (C-m); ligand moiety: 157.85 (>C=O), 146.93 (>C=N), 17.29 (CH_3).

2.1.12. Ph_3SbCl_2(mipkscz). Yield 0.530 g (79.34%), m.p. 86°C, Anal. Calcd for $SbCl_2C_{24}H_{28}N_3O$ (%): Sb, 21.46; Cl, 12.50; C, 50.82; H, 4.97; N, 7.40. Found (%): Sb, 20.99; Cl, 12.80; C, 50.64; H, 4.48; N, 7.10. IR: 3480 cm^{-1} ν_{NH2} asym, 3300 cm^{-1} ν_{NH2} sym, 3050 cm^{-1} ν_{NH}, 1700 cm^{-1} $\nu_{C=O}$, 1580 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 1.0 (d, 7.2 Hz, –CH($\underline{CH_3}$)$_2$, 1.8 (s, –CH_3), 2.4 (m, –$\underline{CH}$(CH_3)$_2$), 5.8 (s, br, NH_2), 7.3–8.6 (m, Ph_3Sb), 8.9 (s, NH). ^{13}C NMR: Ph_3Sb: 142.00 (C-i), 134.75 (C-o), 132.18 (C-p), 130.21 (C-m); ligand moiety: 157.99 (>C=O), 154.00 (>C=N), 36.48, 20.19 (–CH(CH_3)$_2$), 13.94 (CH_3).

2.1.13. $SbCl_3$(*trans*-2-NO_2-cinnamscz). Yield 0.823 g (81.27%), m.p. 95°C, Anal. Calcd for $SbCl_3C_{10}H_{10}N_4O_3$ (%): Sb, 26.34; Cl, 23.00; C, 25.98; H, 2.18; N, 12.11. Found (%): Sb, 26.71; Cl, 22.65; C, 26.44; H, 2.52; N, 11.74. IR: 3475 cm^{-1} ν_{NH2} asym, 3225 cm^{-1} ν_{NH2} sym, 3150 cm^{-1} ν_{NH}, 1665 cm^{-1} $\nu_{C=O}$, 1570 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.9–7.9 (m, $NH_2 + C_6H_4CH{=}CH{-}CH$); 10.3 (s, NH). ^{13}C NMR: 156.64 (>C=O),

147.73 (>C=N), 141.30, 133.70, 130.78, 130.48, 130.05, 129.31, 128.00, 124.78 (–C_6H_4–CH=CH).

2.1.14. $SbCl_3$(salscz). Yield 0.832 g (93.20%), m.p. 106°C, Anal. Calcd for $SbCl_3C_8H_9N_3O_2$ (%): Sb, 24.48; Cl, 12.20; C, 51.66; H, 5.20; N, 7.23. Found (%): Sb, 24.90; Cl, 11.90; C, 51.18; H, 4.98; N, 7.05. IR: 3460 cm^{-1} ν_{NH2} asym, 3350 cm^{-1} ν_{NH2} sym, 3150 cm^{-1} ν_{NH}, 1660 cm^{-1} $\nu_{C=O}$, 1590 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 5.9–7.1 (m, $NH_2 + C_6H_4CH$), 9.8 (s, br, OH + NH). ^{13}C NMR: 157.11 (>C=O), 156.19 (>C=N), 138.84, 130.80, 127.16, 120.41, 119.61, 116.41 (C_6H_4).

2.1.15. $SbCl_3$(cinnamtscz). This compound was prepared as given in the literature [41]. Yield 0.948 g (94.32%).

2.1.16. $SbCl_3$(*trans*-2-NO_2-cinnamtscz). Yield 0.858 g (86.34%), m.p. 98°C, Anal. Calcd for $SbCl_3C_{10}H_{10}N_4SO_2$ (%): Sb, 25.45; Cl, 22.23; C, 25.11; H, 2.10; N, 11.71. Found (%): Sb, 25.80; Cl, 21.75; C, 25.48; H, 2.51; N, 11.33. IR: 3390 cm^{-1} ν_{NH2} asym, 3260 cm^{-1} ν_{NH2} sym, 3198 cm^{-1} ν_{NH}, 740 cm^{-1} $\nu_{C=S}$, 1610 cm^{-1} $\nu_{C=N}$. ^{1}H NMR: 6.8–7.9 (m, $NH_2 + C_6H_4CH$=CH), 8.2 (s, CH), 11.5 (s, NH). ^{13}C NMR: 178.27 (>C=S), 148.16 (>C=N), 134.14, 133.15, 130.92, 130.04, 125.08 (C_6H_4CH=CH).

2.2. *Biological activity*

Representative ligands and their complexes synthesized during the present investigation were screened *in vitro* for antibacterial activity against *Salmonella typhi*, *Pseudomonas aeruginosa*, *Vibrio cholerae*, and *Streptococcus pneumoniae* and for antifungal activity against *Candida albicans* and *Aspergillus niger*, which were clinical isolates from Haffkins Laboratory, Mumbai (India). All the bacterial strains were maintained on nutrient agar (Himedia Lab. Ltd., India) slants and the fungal strains were maintained on Sabouraud's agar (Himedia Lab. Ltd., India) slants at 4°C prior to use for antimicrobial and antifungal susceptibility tests. The bioassays of these complexes were carried out by the agar cup method [44, 45] against all test microorganisms. The measured quantity of culture of the test organism (0.5 mL) was poured into the sterilized Petri plates and then the warm (~55°C) agar media was added into this and the plates were shaken well. The test solutions of 500 and 1000 ppm dilutions of the respective complexes were prepared in DMSO. Four cups of 6 mm diameter were cut in the culture media on the Petri dishes using a sterile metallic borer of 6 mm diameter. Hundred microliters of particular dilutions (500 or 1000 ppm) was introduced into the outer three cups of one of the Petri plates and the second solution was put in the three cups of other Petri plates. Then the central cup of all the Petri plates were filled with the control solution and all the Petri plates were allowed to remain in the refrigerator maintained at ~10°C for ~1 h to allow diffusion of the solution. The plates were incubated at 37°C for 24 h. All the tests were carried out in triplicate and the activity was determined by taking average values of diameters of zones showing complete inhibition in millimeters with an error limit of ±0.1 mm. The control DMSO showed no activity against any bacterial/fungal strains.

2.3. *Pyrolysis in a furnace*

A weighed quantity of the complex was taken in a quartz boat and placed in a horizontal tubular furnace. The temperature of the furnace was then set to a desired value and was maintained at this temperature for 3 h. The decomposition was carried out under nitrogen in order to avoid *in situ* oxidation. After cooling the furnace to room temperature, the black residue obtained was characterized by XRD pattern, SEM, and EDAX.

3. Results and discussion

3.1. *Synthesis and spectroscopy*

The reactions of antimony(V) and (III) chlorides with semi- and thiosemicarbazones in 1 : 1 stoichiometry in dry THF gave molecular adducts $Ph_3SbCl_2(L)$ and $SbCl_3(L)$, respectively (equations 1 and 2).

$$Ph_3SbCl_2 + L \xrightarrow{\text{Dry THF}} Ph_3SbCl_2(L) \quad (1)$$

$$SbCl_3 + L \xrightarrow{\text{Dry THF}} SbCl_3(L) \quad (2)$$

The resulting compounds are colored solids. These compounds were characterized by elemental analyses, IR, ^1H and $^{13}C\{^1H\}$ NMR spectral data, TGA, and conductometric measurements. The elemental analyses matched with 1 : 1 stoichiometry of adducts.

In IR spectra of ligands a strong band at 3225–3500 cm^{-1} is assigned to symmetric and asymmetric stretching of NH_2 [46–48]. These bands remain unaltered in spectra of adducts indicating non-participation of NH_2 in bonding. Bands observed at 2900–3350 cm^{-1} are due to ν_{NH} and ν_{CH}. A band at 1680–1750 cm^{-1} in spectra of semicarbazone ligands is assigned to $\nu_{C=O}$. This shifts to lower wavenumber, 1640–1740 cm^{-1}, in the complexes indicating participation of carbonyl in bonding. A band at ~1620 cm^{-1} in the ligands is assigned due to $\nu_{C=N}$. On complexation this band shifts to lower wavenumber, ~1600 cm^{-1}. In thiosemicarbazone ligands $\nu_{C=S}$ is observed at ~840 cm^{-1}, shifted to lower wavenumber after complexation.

In ^1H NMR spectra, the position of NH_2 does not change much after complexation, indicating non-involvement of NH_2 in bonding. These observations are consistent with ligand coordination through O/S and azomethine nitrogen [22–26].

The low values of conductance of these complexes (10–15 $\Omega^{-1}\,cm^2\,mol^{-1}$) in dry DMF show their non-ionic nature. Based on these observations, heptacoordinate (**I**) and pentacoordinate (**II**) antimony with ligand coordination through oxygen/sulfur and azomethine nitrogen is suggested for these complexes (Figure 1).

3.2. *Biological activity*

3.2.1. Antifungal activity. The antifungal activity of the ligands and their complexes are shown in table 1. The ligands show no activity against both fungal species. The complexes showed no or moderate activity against *C. albicans*. However, they show

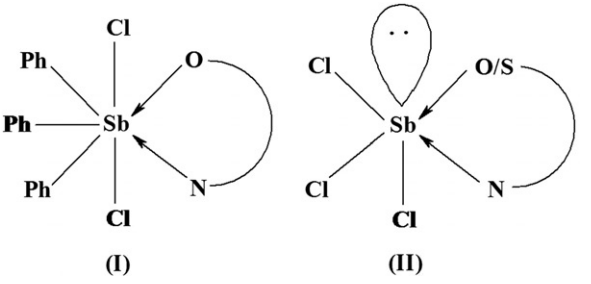

Figure 1. Probable structures of Ph_3 $SbCl_2$ (L) **I** and $SbCl_3$ (L) **II**.

moderate or significant activity against *A. niger*. Compounds **1**, **2**, and **5** showed no or weak activity against both test microorganisms. Compounds **3**, **4**, **6**, **7**, and **8** are moderately active. The semi- and thiosemicarbazone derivatives of antimony(III) are comparatively less active than the semicarbazone derivatives of antimony(V). The antimony(III) thiosemicarbazone complexes show higher activity against *A. niger* than *C. albicans* having moderate or no activity. Thus, all these complexes are more active against *A. niger* than *C. albicans*. The activities of the compounds reported here are moderate compared to the activities of standard, Miconazole [49] (table 1).

3.2.2. Antibacterial activity. The *in vitro* antibacterial activities of representative ligands and their complexes were tested against some Gram-negative (*S. typhi*, *P. aeruginosa*, and *V. cholerae*) and Gram-positive (*S. pneumoniae*) bacteria. As shown in table 2, activity of the ligands is less than their corresponding complexes. Hashmi *et al.* [49] reported similar observations for sulfur-containing ligands and their corresponding organotin(IV) complexes showing weak antibacterial activity of ligands and a moderate activity for complexes. All the complexes are less-active against *V. cholerae*. The activity of Ph_3SbCl_2(*trans*-2-NO_2-cinnamscz) and Ph_3SbCl_2(indol-3-carbscz) was moderate at 1000 ppm against *V. cholerae* and *S. pneumoniae*, but they are completely inactive against the remaining three bacterial strains. Antimony(III) semi- and thiosemicarbazones are comparatively more active than the antimony(V) semicarbazone complexes against all the bacterial strains. The antibacterial activity studies with these bacteria were also carried out with ampicillin and the activities were compared with the antibacterial activities of the compounds reported here. The activities of the compounds reported here are moderate compared to those of ampicillin. However, antibacterial activities of some of the compounds ($SbCl_3$(*trans*-2-NO_2-cinnamscz), $SbCl_3$(cinnamtscz), $SbCl_3$(*trans*-2-NO_2-cinnamtscz), and $SbCl_3$(4-F-acphtscz)) are comparable with the activities of the ampicillin.

3.3. *Thermal studies*

Compounds containing direct metal–chalcogen bonds can act as single molecule precursors for metal chalcogenide materials [50]. We thought it worthwhile to carry out decomposition studies of representative complexes synthesized during the present investigation as they possess direct metal–chalcogen bonds. Thus, the decompositions

Table 1. Antifungal screening data of representative ligands and complexes.

Sr. No.	Compound	Concentration (ppm)	Zone of inhibition (mm)	
			C. albicans	*A. niger*
1	Pyscz	1000	–	–
		500	–	–
2	Salscz	1000	–	–
		500	–	–
3	Cinnamscz	1000	–	–
		500	–	–
4	*trans*-2-NO_2-cinnamscz	1000	–	–
		500	–	–
5	Ind-3-carbscz	1000	–	–
		500	–	–
6	4-Cl-benzscz	1000	–	–
		500	–	–
7	4-F-acphscz	1000	–	–
		500	–	–
8	Acscz	1000	–	–
		500	–	–
9	Cinnamtscz	1000	–	–
		500	–	–
10	*trans*-2-NO_2-cinnamtscz	1000	–	–
		500	–	–
11	4-F-acphtscz	1000	–	–
		500	–	–
12	Ph_3SbCl_2(pyscz)	1000	9	–
		500	–	–
13	Ph_3SbCl_2(salscz)	1000	–	9
		500	–	–
14	Ph_3SbCl_2(cinnamscz)	1000	12	11
		500	8	8
15	Ph_3SbCl_2(*trans*-2-NO_2-cinnamscz)	1000	10	10
		500	7	–
16	Ph_3SbCl_2(ind-3-carbscz)	1000	9	–
		500	–	–
17	Ph_3SbCl_2(4-Cl-benzscz)	1000	10	10
		500	8	7
18	Ph_3SbCl_2(4-F-acphscz)	1000	–	12
		500	–	9
19	Ph_3SbCl_2(acscz)	1000	9	9
		500	–	–
20	$SbCl_3$(*trans*-2-NO_2-cinnamscz)	1000	13	22
		500	10	17
21	$SbCl_3$(salscz)	1000	13	23
		500	–	20
22	$SbCl_3$(cinnamtscz)	1000	12	20
		500	9	16
23	$SbCl_3$(*trans*-2-NO_2-cinnamtscz)	1000	15	23
		500	10	19
24	$SbCl_3$(4-F-acphtscz)	1000	13	22
		500	10	15
25	Miconazole[a]	1000	28	30
		500	21	22

<8 mm = weak activity; 8–16 mm = moderate activity; 17–29 mm = significant activity; – = no zone of inhibition.
[a]Data from ref. [49].

Table 2. Antibacterial screening data of representative ligands and complexes.

Sr. No.	Compound	Conc. (ppm)	Zone of inhibition (mm)			
			S. typhi	*P. aeruginosa*	*S. pneumoniae*	*V. cholerae*
1	Pyscz	1000	–	–	–	7
		500	–	–	–	–
2	Salscz	1000	–	–	–	8
		500	–	–	–	–
3	Cinnamscz	1000	–	–	–	–
		500	–	–	–	–
4	*trans*-2-NO_2-cinnamscz	1000	–	–	–	7
		500	–	–	–	–
5	Ind-3-carbscz	1000	–	–	–	–
		500	–	–	–	–
6	4-Cl-benzscz	1000	–	–	–	7
		500	–	–	–	–
7	4-F-acphscz	1000	–	–	–	–
		500	–	–	–	–
8	Acscz	1000	–	–	–	7
		500	–	–	–	–
9	Cinnamtscz	1000	7	–	–	–
		500	–	–	–	–
10	*trans*-2-NO_2-cinnamtscz	1000	–	–	–	–
		500	–	–	–	–
11	4-F-acphtscz	1000	–	–	–	–
		500	–	–	–	–
12	Ph_3SbCl_2(pyscz)	1000	10	10	10	9
		500	–	–	–	–
13	Ph_3SbCl_2(salscz)	1000	11	10	11	11
		500	7	–	8	7
14	Ph_3SbCl_2(cinnamscz)	1000	11	12	11	10
		500	7	8	8	–
15	Ph_3SbCl_2(*trans*-2-NO_2-cinnamscz)	1000	–	–	–	11
		500	–	–	–	7
16	Ph_3SbCl_2(ind-3-carbscz)	1000	–	–	9	–
		500	–	–	–	–
17	Ph_3SbCl_2(4-Cl-benzscz)	1000	–	11	9	9
		500	–	8	–	–
18	Ph_3SbCl_2(4-F-acphscz)	1000	–	10	11	–
		500	–	7	7	–
19	Ph_3SbCl_2(acscz)	1000	12	10	9	9
		500	9	7	–	–
20	$SbCl_3$(*trans*-2-NO_2-cinnamscz)	1000	27	20	12	25
		500	11	12	10	10
21	$SbCl_3$(salscz)	1000	23	12	12	–
		500	–	10	11	–
22	$SbCl_3$(cinnamtscz)	1000	28	22	12	10
		500	13	14	11	–
23	$SbCl_3$(*trans*-2-NO_2-cinnamtscz)	1000	25	25	14	10
		500	13	14	11	9
24	$SbCl_3$(4-F-acphtscz)	1000	29	25	14	11
		500	13	14	12	9
25	Ampicillin	1000	20	18	18	17
		500	18	15	14	14

<8 mm = weak activity; 8–16 mm = moderate activity; 17–29 mm = significant activity; – = no zone of inhibition.

of Ph_3SbCl_2(L) (L = 4-fluoroacetophenone semicarbazone (4-F-acphscz)) and $SbCl_3$(L) (L = 4-fluoroacetophenone thiosemicarbazone (4-F-acphtscz)) were carried out. TGA of these complexes show that total weight loss of Ph_3SbCl_2(4-F-acphscz) and $SbCl_3$(4-F-acphtscz) obtained from TGA agree well with the calculated weight loss for the formation of Sb (Calcd 80.34%, Obs. 79.96%) and Sb_2S_3 (Calcd 61.34%, Obs. 68.00%), respectively. The former complex showed single-step decomposition at 310°C, whereas the latter at 350°C. More weight loss for the latter complex may be due to the formation of slightly sulfur deficient Sb_2S_3, which was also observed in the decomposition experiment of this complex. The decomposition of Ph_3SbCl_2(4-F-acphscz) was carried out at 500°C, whereas decomposition of $SbCl_3$(4-F-acphtscz) was carried out at 350°C. The XRD pattern of the material obtained from decomposition of Ph_3SbCl_2(4-F-acphscz) match with the rhombohedral Sb (JCPDS: 85-1324; Figure S1a) and the XRD pattern of the decomposition product of $SbCl_3$(4-F-acphtscz) match with orthorhombic Sb_2S_3 (JCPDS: 73-0393; Figure S1b). The EDAX analysis revealed the formation of 100% Sb from the decomposition of Ph_3SbCl_2(4-F-acphscz). The Sb : S ratio is found to be 1 : 1.35 for the material obtained from $SbCl_3$(4-F-acphtscz).

The SEM images (Figures S2a and S2b) of the material obtained from Ph_3SbCl_2(4-F-acphscz) showed sheet-like morphology and that of the material obtained from $SbCl_3$(4-F-acphtscz) has rod-like morphology.

4. Conclusion

Antimony(III) and (V) semi- and thiosemicarbazone complexes have been synthesized and characterized. They show antibacterial and antifungal activity against various bacterial and fungal strains. Thermal decomposition of Ph_3SbCl_2(L) and $SbCl_3$(L) gave micron-size Sb and Sb_2S_3 particles, respectively. Thus, these complexes have biological activity and can also be used as single-source precursors to obtain inorganic materials.

Acknowledgments

Thanks are due to SAIF, IIT-Bombay for providing NMR spectra of the complexes, TIFR, Mumbai for SEM images and EDAX data.

References

[1] D.X. West, S.B. Padhye, P.B. Sonawane. *Struct. Bond.*, **76**, 1 (1991).
[2] R.B. Singh, H. Ishii. *Crit. Rev. Anal. Chem.*, **22**, 381 (1991).
[3] R.B. Singh, B.S. Garg, R.P. Singh. *Talanta*, **25**, 619 (1978).
[4] S.B. Padhye, G.B. Kaufman. *Coord. Chem. Rev.*, **63**, 127 (1985).
[5] D.L. Klayman, J.P. Scovill, J.F. Bartosevich, J. Bruce. *J. Med. Chem.*, **26**, 35 (1983).
[6] J.S. Casas, M.S. Garcia-Tasende, J. Sordo. *Coord. Chem. Rev.*, **209**, 197 (2000).
[7] K.N. Thimmaiah, G.T. Chandrappa, Rangaswamy, Jayarama. *Polyhedron*, **3**, 1237 (1984).
[8] D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar, R.G. Yerande. *Coord. Chem. Rev.*, **123**, 49 (1993).

[9] U. Abram, K. Ortner, K. Somma. *J. Chem. Soc., Dalton Trans*., 735 (1999).
[10] R. Diemer, U. Dittes, B. Nuber, V. Seifried, W. Opferkuch, B.K. Keppler. *Met.-Based Drugs*, **2**, 271 (1995).
[11] D.X. West, G.A. Bain, R.J. Butcher, J.P. Jasinski, Y. Li, R.Y. Pozdniakiv, J. Valdes-Martinez, R.A. Toscano, S. Hernandes-Ortega. *Polyhedron*, **15**, 665 (1996).
[12] D. Kovala-Demertzi, A. Domopoulou, M. Demertzis, C.P. Paptopoulou, A. Terzis. *Polyhedron*, **13**, 1917 (1994).
[13] Z.H. Chohan, H. Pervez, K.M. Khan, C.T. Supuran. *J. Enzyme Inhib. Med. Chem*., **20**, 81 (2005).
[14] M.B. Ferrari, G. Fava, C. Pelizzi, P. Tarasani. *J. Chem. Soc., Dalton Trans*., 2153 (1992).
[15] R.K. Agarwal, L. Singh, D.K. Sharma. *Bioinorg. Chem. Appl*., **2006**, 1 (2006).
[16] G. Ibrahim. *Transition Met. Chem*., **27**, 34 (2002).
[17] G. Ibrahim, E. Chebli. *Transition Met. Chem*., **24**, 294 (1999).
[18] Kiran, R.V. Singh, J.P. Tandon. *Synth. React. Inorg. Met-Org. Chem*., **16**, 1341 (1986).
[19] M. Nath, N. Sharma, C.L. Sharma. *Synth. React. Inorg. Met-Org. Chem*., **19**, 339 (1989).
[20] V.K. Arora, K.B. Pandeya, R.P. Singh. *J. Indian Chem. Soc*., **56**, 656 (1979).
[21] P.L. Maurya, B.V. Agarwala, A.K. Dey. *J. Indian Chem. Soc*., **57**, 275 (1980).
[22] K. Singh, J.P. Tandon. *Monatsh. Chem*., **123**, 315 (1992).
[23] K. Singh, J.P. Tandon. *Monatsh. Chem*., **123**, 983 (1992).
[24] A. Phor. *Synth. React. Inorg. Met. Org. Chem*., **25**, 1685 (1995).
[25] K. Dalvi, M. Pal, S.S. Garje. *Indian J. Chem*., **43A**, 1667 (2004).
[26] N.V. Sawant, S.S. Garje. *Main Group Met. Chem*., **28**, 213 (2005).
[27] G. Ghosh, B.P. Varma. *Thin Solid Films*, **60**, 61 (1979).
[28] B.B. Nayak, H.N. Acharya, G.B. Mitra, B.K. Mathur. *Thin Solid Films*, **105**, 17 (1983).
[29] D. Arivuoli, F.D. Gnanam, P. Ramasamy. *J. Mater. Sci. Lett*., **7**, 711 (1988).
[30] M.E. Rincon, R. Suarez, P.K. Nair. *J. Phys. Chem. Solids*, **57**, 1947 (1996).
[31] L.R. Windmiller. *Phys. Rev*., **149**, 472 (1966).
[32] A.L. Prieto, M.M. Gonzalez, J. Keyani, R. Gronsky, T. Sands, A.M. Stacy. *J. Am. Chem. Soc*., **125**, 2388 (2003).
[33] J.D. Smith. In *Comprehensive Inorganic Chemistry*, Vol. 2, Chap. 21, p 547, Pergamon Press, Oxford, (1973).
[34] D. Cope. U.S. Patent No. 2875, 359 (1959).
[35] J. Grigas, J. Meshakanskas, A. Orliukas. *Phys. Status Solidi A*, **37**, K39 (1976).
[36] E. Montrimass, A. Pazera. *Thin Solid Films*, **34**, 65 (1976).
[37] M.S. Albova, A.A. Andreev, T.T. Degegkaev, B.T. Melekh, A.B. Pevtsov, N.S. Shendel, L.N. Shurnilova. *Sov. Phys. Semicond*., **10**, 6 (1976).
[38] P. Arun, A.G. Vedeshwar, N.C. Mehra. *Mater. Res. Bull*., **32**, 907 (1997).
[39] O. Savadogo, K.C. Mandal. *Solar Energy Mater. Solar Cells*, **26**, 117 (1992).
[40] M.T.S. Nair, Y. Pena, J. Campos, V.M. Garcia, P.K. Nair. *J. Electrochem. Soc*., **145**, 2113 (1998).
[41] J.B. Biswal, N.V. Sawant, S.S. Garje. *Thin Solid Films*, **518**, 3164 (2010).
[42] A.I. Vogel. *Vogel's Textbook of Practical Organic Chemistry*, 5th Edn, ELBS Longman, London (1989).
[43] F.E. Anderson, C.J. Duca, J.V. Scudi. *J. Am. Chem. Soc*., **73**, 4967 (1951).
[44] D.F. Spooner, G. Skyes. In *Methods of Microbiology*, J.R. Norris, D.W. Ribbons (Eds), Vol. 7B, pp. 217–224, Academic Press, London (1972).
[45] S.B. Rose, R.E. Miller. *J. Bacteriol*., **38**, 525 (1939).
[46] P. Dixit, J.P. Tandon. *Indian J. Chem*., **27A**, 153 (1988).
[47] A. Varshney, J.P. Tandon, A.J. Crowe. *Polyhedron*, **5**, 739 (1986).
[48] T.T. Bamgboye. *Inorg. Chim. Acta*, **145**, 243 (1988).
[49] R.K. Joshi, N. Ahmad, S.A. Khan, A.A. Hashmi. *J. Coord. Chem*., **63**, 906 (2010).
[50] A.C. Jones, P. O'Brien. *CVD of Compound Semiconductors: Precursor Synthesis, Development and Applications*, VCH, Weinheim (1997).