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Title: Structural investigation on toluene–3,4–dithiolatoantimony(III) alkyldithiocarbonate complexes: thermal, powder XRD and biological studies

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Abstract

Toluene–3,4–dithiolatoantimony(III) complexes with alkyldithiocarbonates of the type $CH_3(C_6H_3)S_2SbS_2COR$ [where R = CH_3 (**1**), C_2H_5 (**2**), $^{i}C_3H_7$ (**3**), $^{n}C_3H_7$ (**4**), $^{i}C_4H_9$ (**5**) and $^{n}C_4H_9$ (**6**)] have been synthesized by the reaction of toluene–3,4–dithiolatoantimony(III) chloride with potassium alkyldithiocarbonates in 1:1 molar stoichiometry. The nature of bonding of dithiocarbonate ligand to antimony metal is anisobidentate, shown by IR and carbon resonance (^{13}C NMR) spectral analyses. These complexes have nano ranged particle size (4.39–7.29 nm) and lower (monoclinic) symmetry crystal system supports the distorted geometry of synthesized complexes. After thermal decomposition of these types of complexes in an inert atmosphere, we have obtained antimony sulfide as a final thermal decomposition product. It was further accomplished by SEM and EDAX studies. Toluene–3,4–dithiol ligand has strong chelating nature than xanthate ligand which has been confirmed by ESI mass spectra. The antimony to sulfur bond have been shown greater antimicrobial activities than free ligands and standard drugs (chloramphenicol or terbinafine).

Keywords: ^{1}H and ^{13}C NMR, anisobidentate, thermal, powder XRD, ESI–mass, antimicrobial study

Introduction

Research in the field of group 15 metal complexes with mixed sulfur donor ligands have increased significant over the last few decades because of these complexes contain various type of sulfur donor ligands such as 1,1–dithiolato ligands[1a] (alkyldithiocarbonates, dialkyldithiocarbamates etc.) as well as 1,2–dithiolato ligands[1] (toluene–3,4–dithiolates, ethane–1,2–dithiolates etc.) which show attractive structural behavior due to the presence of a stereochemically active lone pair of electrons, smaller ligand bite as well as supramolecular association and show variety of applications in different fields. Dithiocarbonates have wide range of applications in soil conditioning[2] and in controlled radical polymerization process.[3] It has also used in the removal of heavy metals such as Cd, Cu etc. from industrial waste water due to their good adsorbent property and low cost.[4-7] Metal alkyl xanthates have also been used as a precursor in the formation of high quality metal sulfide nanoparticles.[8] On the other hand antimony(III) containing complexes are used to treat parasitic infections such as leishmaniasis[9,10] and also display anti–tumor activity against mice inoculated with S180 solid tumors.[11] Organoantimony compounds reveal good antitumor activity against ehrlich ascites tumor cell lines[12-15] and reported in chemotherapy[16-18], antimicrobial[15] and anticancer activities.[18] One important property of mixed sulfur donor antimony(III) complexes is that it obtained antimony sulfide (stibnite) as a final product on thermal decomposition. The antimony sulfide has many potential applications in various fields such as thermoelectric cooling technologies, solar energy conversion, optoelectronic devices and microwave devices due to its semiconducting property.[19,20]

Our investigations presented in this article are focused on synthetic, physicochemical [melting points, molecular weight determinations, elemental analyses (C, H, S, and Sb)],

spectroscopic [UV, IR, Far–IR and NMR (^{1}H and ^{13}C)] characterization, thermogravimetric analyses (TG and DTG) and powder X–ray diffraction of toluene–3,4–dithiolato antimony(III) alkyldithiocarbonate complexes. These have also screened against four human pathogenic bacterial and two plants fungal species for their antimicrobial activities and compared with the standard drug (chloramphenicol or terbinafine).

Experimental

Materials and Methods

Stringent precautions have been taken to exclude atmospheric moisture throughout the experimental manipulations owing to moisture sensitive nature of the starting materials as well as the newly synthesized compounds. Antimony(III) chloride (E. Merck) was distilled before use. Toluene–3,4–dithiol (Sigma Aldrich) was used as received without further purification. Solvents (acetone, carbon disulfide, dichloromethane, chloroform etc.) were received from E. Merck and purified using standard methods.[36] Reactants toluene–3,4–dithiolato antimony(III) chloride and potassium organodithiocarbonate have been prepared using reported methods.[24,25,37]

Physical Measurements

Microanalyses of carbon and hydrogen have been carried out on a Euro Vector Analyzer at the Sophisticated Analytical Instrumentation Facility (SAIF), CDRI, Lucknow, India. Electronic spectra of the all antimony(III) compounds have been analysed in chloroform solution using Shimadzu UV–1700 UV–Vis. spectrophotometer within a range of 400–200 nm. Infrared spectra have been recorded on a Spectrum BX Series in the range of 4000–400 cm $^{-1}$and far–IR spectra have been recorded as a nujol mull over CsI disks using a Magna–IR Spectrophotometer–550 instrument in the range of 600–50 cm^{-1}. NMR spectra have been recorded in $CDCl_3$ solution on a Bruker Avance II 400 NMR spectrometer, operated at 400.13 & 100.62 MHz for ^{1}H and ^{13}C

respectively, using TMS as standard. Thermal analyses (TG and DTG) have been carried out in an inert atmosphere (N_2 gas flow) on METTLER Toledo model STAR^e SW 8.10 instrument using alumina crucible, over the temperature range 30–600°C with 10°C min^{-1} heating rate, the mass of samples 8.45, 11.30 and 8.66 mg for compound **1**, **3** and **5** respectively. Powder X–ray diffraction patterns of a few compounds have been collected in the 2θ range 5–60° using Bruker D8 Advance X–ray diffractometer using Cu–Kα radiation at a wavelength of 1.54 Å and X–rays have been detected using a fast counting detector based on silicon strip technology (Bruker LynxEye detector) and SEM studies performed on a Jeol JSM 5600 having magnification range x1800–10 μm and x5000–5 μm and at accelerating voltage of 20 kV. The electrospray mass spectra have been recorded using Waters UPLC–TQD Triple Quadrupole mass spectrometer with the capillary voltage 3.5 kV; flow rate 100 μl/min; source and desolvation temperature 120 and 350°C respectively and nitrogen was used as a desolvation gas at a pressure of 100psi. Antimony has been analysed iodometrically and sulfur has been estimated gravimetrically as barium sulphate.[36] Melting points have been determined on a B10 Tech India melting point apparatus. Molecular weights have been determined using cryoscopic method.

Syntheses of Compound 1–6

Toluene–3,4–dithiolatoantimony(III) isopropyldithiocarbonate (compound **3)** was prepared by the addition of acetone solution of toluene–3,4–dithiolatoantimony(III) chloride (1.5g, 4.8mmol) and ligand potassium isopropyl dithiocarbonate (0.84g, 4.8mmol) in 1:1 molar ratios and content was stirred for ~ 4 hrs at room temperature. After that precipitate KCl was removed through filter funnel. Solvent was stripped using reduced pressure and obtained orange yellow solid which was recrystallized using dichlolomethane. All the other complexes were synthesized adopting similar method.

Compound 1

Yield 95 %; orange yellow solid; M.P. 80ºC; MW found (calc.) 379 (383); Anal. Calcd. for $C_9H_9OS_4Sb$ (%): C 28.12, H 2.37, S 33.47, Sb 31.78; found (%): C 27.90, H 2.20, S 33.15, Sb 31.58; UV λ_{max} (nm): 235–255, 309, 365; IR (KBr cm^{-1}): 1214, 1153, 1041, 806, 315; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 4.09 (s, 3H), 6.73 (d, *J* = 7.9 Hz, 1H), 7.14 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.05, 60.39, 124.70, 129.11, 129.72, 133.00, 138.49, 141.95, 221.70.

Compound 2

Yield 92 %; orange yellow sticky solid; MW found (calc.) 387 (397); Anal. Calcd. for $C_{10}H_{11}OS_4Sb$ (%): C 30.24, H 2.79, S 32.29, Sb 30.65; found (%): C 29.90, H 2.72, S 31.92, Sb 30.56; UV λ_{max} (nm): 227–258, 312, 364; IR (KBr cm^{-1}): 1218, 1158, 1038, 802, 318; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, *J* = 7.1 Hz, 3H), 2.20 (s, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 6.72 (d, *J* = 7.9 Hz 1H), 7.17 (s, 1H), 7.28 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.27, 20.23, 70.91, 125.53, 128.83, 129.53, 133.12, 138.01, 139.99, 219.41.

Compound 3

Yield 94 %; orange yellow solid; M.P. 92ºC; MW found (calc.) 403 (411); Anal. Calcd. for $C_{11}H_{13}OS_4Sb$ (%): C 32.13, H 3.19, S 31.19, Sb 29.61; found (%): C 31.95, H 3.10, S 30.89, Sb 29.48; UV λ_{max} (nm): 220–227, 310, 367; IR (KBr cm^{-1}): 1221, 1138, 1045, 804, 315; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (d, *J* = 6.2 Hz, 6H), 2.28 (s, 3H), 5.51–5.54 (m, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 7.23 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.40, 21.40, 80.79, 125.96, 129.77, 130.49, 134.81, 137.70, 141.19, 219.56.

Compound 4

Yield 90 %; orange yellow sticky solid; MW found (calc.) 405 (411); Anal. Calcd. for $C_{11}H_{13}OS_4Sb$ (%): C 32.13, H 3.19, S 31.19, Sb 29.61; found (%): C 32.06, H 3.12, S 31.12, Sb 29.31; UV λ_{max} (nm): 237–255, 310, 366; IR (KBr cm^{-1}): 1208, 1148, 1041, 806, 320; ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, *J*=6.6 Hz, 3H), 1.73–1.86 (m, 2H), 2.27 (s, 3H), 4.45 (t, *J* = 6.6 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 7.23 (s, 1H), 7.29 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.52, 20.93, 21.04, 77.51, 125.99, 129.78, 130.52, 134.87, 137.67, 141.14, 220.70.

Compound 5

Yield 96 %; orange yellow solid; M.P. 85ºC; MW found (calc.) 418 (425); Anal. Calcd. for $C_{12}H_{15}OS_4Sb$ (%): C 33.89, H 3.56, S 30.16, Sb 28.63; found (%): C 33.51, H 3.21, S 29.81, Sb 28.58; UV λ_{max} (nm): 232–251, 311, 361; IR (KBr cm^{-1}): 1221, 1170, 1037, 808, 318; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.6 Hz, 6H), 1.97–2.04 (m, 1H), 2.16 (s, 3H), 4.19 (d, *J* = 6.6 Hz, 2H), 6.64 (d, *J* = 7.9 Hz, 1H), 7.07 (s, 1H), 7.12 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.89, 20.07, 30.37, 80.27, 124.88, 129.10, 129.73, 133.32, 138.02, 141.48, 220.20.

Compound 6

Yield 95 %; orange yellow sticky solid; MW found (calc.) 420 (425); Anal. Calcd. for $C_{12}H_{15}OS_4Sb$ (%): C 33.89, H 3.56, S 30.16, Sb 28.63; found (%): C 33.57, H 3.40, S 30.05, Sb 28.41; UV λ_{max} (nm): 229–248, 307, 360; IR (KBr cm^{-1}): 1215, 1165, 1038, 802, 320; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.6 Hz, 3H), 1.28–1.40 (m, 2H), 1.51–1.71 (m, 2H), 2.30 (s, 3H), 4.41 (t, *J* = 6.6 Hz, 2H), 6.70 (d, *J* = 7.9 Hz, 1H), 7.15 (s, 1H), 7.21 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.85, 19.57, 20.24, 33.87, 74.84, 124.92, 128.73, 129.45, 133.61, 136.81, 140.15, 219.60.

The ESI mass spectra of the compound **1** and **3** are shown in the Fig. S4 and S5. The possible formulae of fragments and their m/z ratios are as follows:

Compound 1

382.2 (16) $[M]^+$, 381.2 (78) $[M–H]^+$, 353.1 (8) $[M–C_2H_5]^+$, 341.2 (7) $[M–C_3H_5]^+$, 278.7 (7) $[M–C_7H_3O]^+$, 276.7 (91) $[M–C_2HOS_2]^+$, 274.7 (100) $[M–C_2H_3OS_2]^+$, 245.9 (3) $[M–C_4H_8OS_2]^+$, 228.7 (6) $[M–C_4H_9OS_{2.5}]^+$, 198.7 (13) $[M–C_8H_7OS_2]^+$, 171.7 (8) $[M–C_9H_6OS_{2.5}]^+$.

Compound 3

383.2 (8) $[M–C_2H_4]^+$, 381.2 (32) $[M–C_2H_5]^+$, 353.0 (6) $[M–C_3H_5O]^+$, 278.8 (4) $[M–C_4H_3OS_2]^+$, 277.7 (8) $[M–C_4H_4OS_2]^+$, 276.7 (77) $[M– C_4H_5OS_2]^+$, 274.7 (100) $[M–C_4H_7OS_2]^+$, 246.7 (5) $[M–C_6H_{11}OS_2]^+$, 228.7 (9) $[M–C_{10}H_{13}OS]^+$, 196.8 (8) $[M–C_{10}H_{13}OS_2]^+$.

Antimicrobial Studies

Test microorganism strains

Test strain of four human pathogenic bacterial species, two Gram–positive [*Staphylococcus aureus* (ATCC 9144) (G+) and *Bacillus subtilis* (ATCC 6051) (G+)] and two Gram–negative [*Escherichia coli* (ATCC 9637) (G−) and *Pseudomonas aeruginosa* (ATCC 25619) (G−)] and two plant fungal species [*Aspergillus niger* (ATCC 9029) and *Penicilium chrysogenum* (ATCC 10106)] were screened for their *in vitro* antimicrobial studies using the well diffusion method.

Method

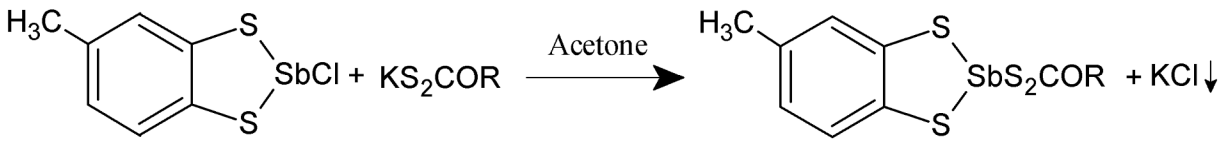
The compounds were screened for their *in vitro* antimicrobial studies by the well diffusion method.[24,38,39] The compound was dissolved in DMF to obtain a 200–μg mL^{-1} solution. Further progressive double dilutions were performed to obtain the required concentrations of 100 and 50 μg mL^{-1}. At first nutrient agar media and broth were prepared in the required amounts. The

investigated microorganism cultured in broth and for growing the bacteria incubated at 37°C for 24 hrs. After incubation clear broth solution changed in tarbid solution due to the bacterial growth. Now 0.5 mL of this tarbid solution of the broth was spread into the sterile Petri plate, then sterile nutrient agar was poured into broth containing Petri plates (12 cm in diameter) and left to solidify. Using a sterile cork borer (6 mm in diameter), three holes were made in each dish and then 0.1 mL of the tested compound dissolved in DMF (50, 100 and 200 μg mL^{-1}) was poured into these holes. Finally the Petri dishes were incubated at 37°C for 24 hrs. Distinct or light inhibition zones were observed, around each hole, which were measured in millimeters as the diameter of inhibition zones by taking the mean Dimethyl formamide (DMF) exhibiting no effect on the organism tested.

Results and Discussion

Synthesis

In the acetone solution of toluene–3,4–dithiolato antimony(III) chloride, potassium salt of alkyldithiocarbonats was mixed in 1:1 molar ratios at room temperature shown in Scheme 1.



Scheme 1 Syntheses of toluene–3,4–dithiolatoantimony(III) alkyldithiocarbonate complexes (where R = CH_3, C_2H_5, $^{i}C_3H_7$, $^{n}C_3H_7$, $^{i}C_4H_9$, $^{n}C_4H_9$)

UV–Visible Spectral analysis

The important bands of these complexes have been assigned on the basis of earlier publications.[21,22] First intense band appeared in the range 220–258 nm due to intramolecular π – π* transition of toluene–3,4–dithiolato moiety. Second band observed between 307 and 312 nm and is attributed to π – π* transition of SCS group of the xanthate moiety. Third band also observed as a shoulder band in the range 360–367 nm due to weak intensity n – π* transition.

FT–IR and Far–IR Spectral analyses

Bands appeared in the region 1208–1221 cm^{-1} and 1138–1170 cm^{-1} due to asymmetric stretching vibration of C–O bond in OCS_2 group of the xanthate moiety.[22,23] The strong–intense band due to thiocarbonyl υ(C–S) group observed at 1037–1045 cm^{-1} region, indicates the bidendate nature of xanthate ligand.[23,24] The band attributed to tri–substituted benzene ring has been observed in the range 802–808 cm^{-1}.[25,26] Another band, which is confirm the bonding of antimony to sulfur, appeared in the lower frequency region 315–320 cm^{-1} is attributed to υ(Sb–S).[27,28]

^{1}H and ^{13}C NMR Spectral analyses

All the complexes have shown a sharp singlet signal in the chemical shift (δ) 2.16–2.30 ppm due to ring CH_3 protons of toluene moiety. Another singlet peak appeared in the range 7.07–7.23 ppm which is attributed to ring C–2 proton. Two doublet proton resonances have also been exhibited in the region 6.64–6.79 and 7.12–7.30 ppm for ring C–6 and C–5 protons respectively. In addition, Different alkyl groups of dithiocarbonates show expected signals due to their respective moieties (Fig. S1 and S3).

In order to assign the ^{13}C NMR signals, we assumed that higher intensity signal observed at 20.05–20.98 ppm due to ring CH_3 carbon. Three carbon resonances of nonprotonated ring carbons C–1, C–3 and C–4 have lower intensity and higher frequency than protonated ring carbons C–2, C–5 and C–6.[29] The peak of thio carbon containing OCS_2 group is shifted towards in the region 219.41–221.70 ppm, which indicates the anisobidentate nature of xanthate ligand[30] (see Fig. S2 and S4).

Powder X-ray diffraction

Powder XRD data of the complexes **1**, **3** and **5** are concisely in Table S1–S3 and diffracted plots are given in Fig. 1–3. These complexes have monoclinic crystal system with unit cell volume V

= 2517 (**1**), 2476 (**3**) and 11060 (**5**) $Å^3$ respectively. Average crystallite size has been calculated using Debye–Scherrer formula:[31,32]

$$D = \frac{K\lambda}{B\ \cos\theta}$$

Where, *D* = particle size, *K* = is a constant (value = ~0.9), λ = wavelength, *B* = full width at half–maximum (FWHM) and θ = Bragg angle. The crystallite particle size of the complexes obtained in the nano ranged (4.39–7.29 nm) with lower (monoclinic) symmetry crystal system. The interplanar *d*– spacing and unit cell volume have been calculated using following formula:[32]

$$\frac{1}{d^2} = \frac{1}{sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2 sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hkl\ cos\beta}{ac}\right)$$

$$V = abc\sin\beta$$

The interplanar *d*– spacing values of these complexes have been matched which is equal and sometime nearly matches with the standard diffraction database JCPDS card numbers 00–034–1835, 00–085–0970 and 00–048–2408. Qualitative phase analyses of these complexes have been performed by comparing the experimental values of the interplanar *d*– spacing and relative intensities with standard diffraction patterns and finally conclude that the complexes are biphasic material, this is due to antimony(III) compounds are mixed ligand complexes.

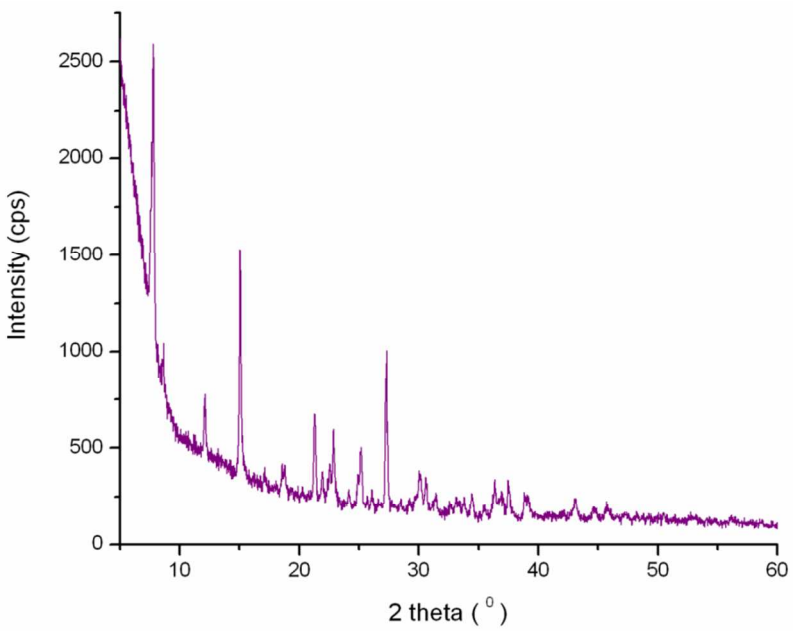


Fig. 1 Powder XRD pattern of toluene–3,4–dithiolatoantimony(III) methyldithiocarbonate (compound 1).

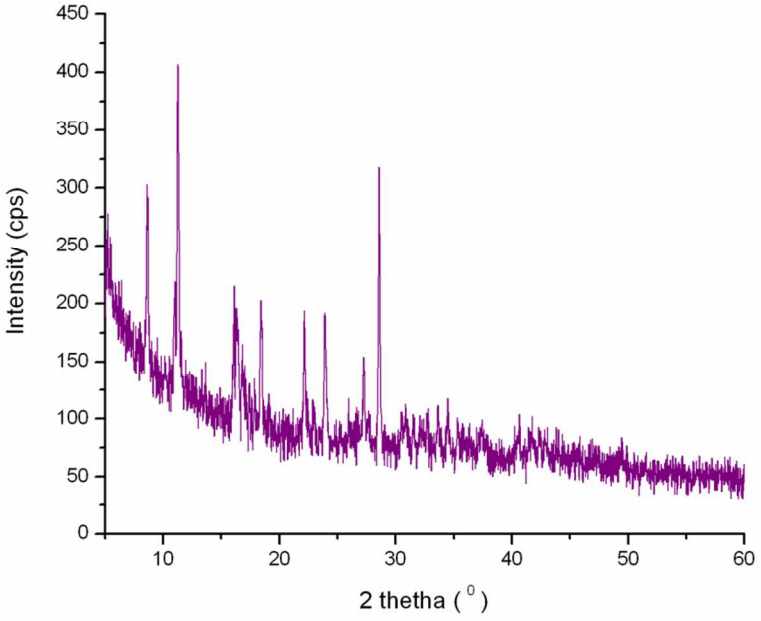


Fig. 2 Powder XRD pattern of toluene–3,4–dithiolatoantimony(III) isopropyldithiocarbonate (compound 3).

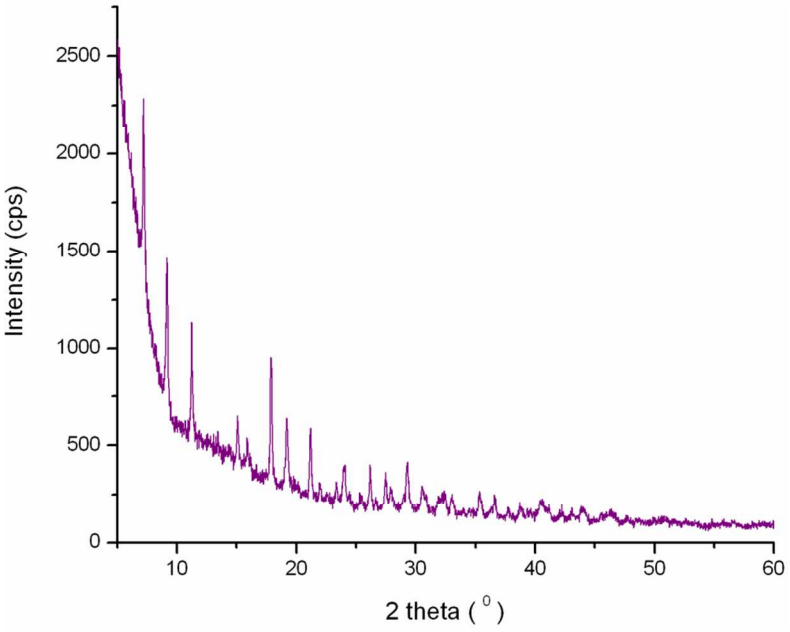


Fig. 3 Powder XRD pattern of toluene–3,4–dithiolatoantimony(III) isobutyldithiocarbonate (compound 5).

Structural Elucidation

Carbon resonance signal of these complexes due to OCS_2 group at 219.41–221.70 ppm reveals the anisobidentate mode of binding of dithiocarbonate moiety. Bidentate nature of the same ligand has been shown by stretching vibrational frequency of thiocarbonyl group (C–S) observed at 1037–1045 cm^{-1}. The antimony metal to sulfur atom bonding confirmed by υ(Sb–S) in the region 315–320 cm^{-1}. By all the obtained results, we conclude that the antimony(III) complexes adopt distorted trigonal bipyramidal geometry (Fig. 4) and stereochemically active lone pair of electron occupy at the corner of trigonal (equatorial) position. In addition, powder XRD studies show that nano–ranged particle size (4.39–7.29 nm) and monoclinic crystal system of the complexes which also support the lower symmetry system.

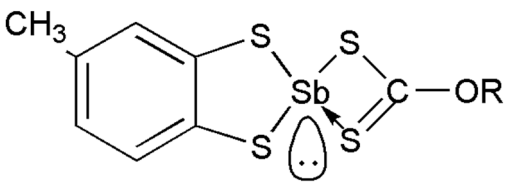


Fig. 4 Proposed structure of the complexes.

Thermogravimetric analyses

The thermogravimetric analyses[22] of compound **1**, **3** and **5** have been summarized in Table 1. Thermograms of compound **1** shows four steps and compound **3** and **5** show three steps of weight loss as shown in Fig. 5, 6 and 7, respectively.

First decomposition step of compound **1** (Fig. 5) is related 2.35 % weight loss, which was occurred in the temperature range 32–138ºC and second step corresponds to the removal of 12.81 % (C_3H_4 part) of the compound taken place in between 145 and 292ºC. The second last step of weight losses indicate the elimination of $C_6H_3S_2$ fragment, with the expected (37.34 %) and calculated (36.33 %) values of weight losses and the final step corresponds to the degradation of S_3 ($^1/_6$ part) with subsequent formation of $½Sb_2S_3$ in the temperature range 525–600ºC. It was also supported by their observed (45.14 %) and calculated (44.33 %) values of remaining material.

For compound **3** (Fig. 6), the curve starts from 30ºC and continuously decomposed till 250ºC. This decomposition step corresponds to the removal of the 28.74 % organic part ($C_5H_{10}O$) of compound. Next step (258–478ºC) indicates the elimination of C_6H_3 and $¼S_3$ moieties with expected (23.62 %) and calculated (24.11 %) weight losses. The final step of weight loss occurs in the temperature range 488–600ºC by the elimination of $¼S_3$ and we get antimony sulfide as a remaining material which also confirmed by expected (40.56 %) and experimental (41.30 %) remaining percentage mass values.

In case of compound **5**, three steps of mass losses shown in Fig. 7. First step (30–230ºC) related to the removal of the organic part of the compound with the expected (27.97 %) and calculated (27.58%) results. The next thermal decomposition step indicates the elimination of C_7H_6S moiety (28.73 %) in the temperature range 237–480ºC and antimony sulfide was

remained in the last step (490–600ºC) by the removal of $^{1}/_{6}S_3$. The expected and calculated values are 40.77 and 39.92 % respectively, which also confirm the formation of antimony sulfide.

The derivative thermogravimetric (DTG) results have also been shown corresponding temperature range of evolution profiles and support the thermogravimetric (TG) analyses. For compound **1, 3** and **5** peaks observed at 128 and 370ºC; 170, 360 and 568ºC; 135 and 360ºC respectively. In each case intense peaks have been obtained that is indicates the high reactivity of the complexes to form the antimony sulfide.

Table 1. Thermogravimetric analysis of toluene–3,4–dithiolatoantimony(III) alkyldithiocarbonates

Compound No.	Steps	Decomposition temp. range (°C)	Mass losses (%) found (calc.)	DTG peaks
1[a]	I	32 – 138	1.95 (2.35)	128
	II	145 – 292	11.59 (12.81)	370
	III	295 – 518	37.34 (36.33)	
	IV	525 – 600	3.98 (4.18)	
3[b]	I	30 – 250	29.72 (28.74)	170
	II	258 – 478	23.62 (24.11)	360
	III	488 – 600	6.10 (5.85)	568
5[c]	I	30 – 230	27.97 (27.58)	135
	II	237 – 480	28.04 (28.73)	360
	III	490 – 600	3.22 (3.77)	
[a] Remaining material ½ Sb_2S_3 (%) found (calc.) = 45.14 (44.33)				
[b] Remaining material ½ Sb_2S_3 (%) found (calc.) = 40.56 (41.30)				
[c] Remaining material ½ Sb_2S_3 (%) found (calc.) = 40.77 (39.92)				

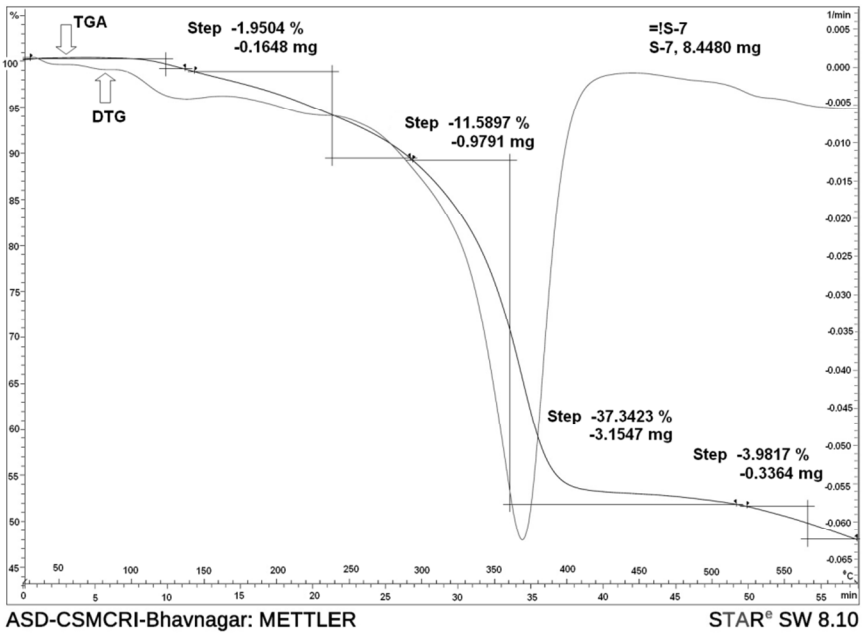


Fig. 5 TG and DTG curve of toluene–3,4–dithiolatoantimony(III) methyldithiocarbonate (compound 1).

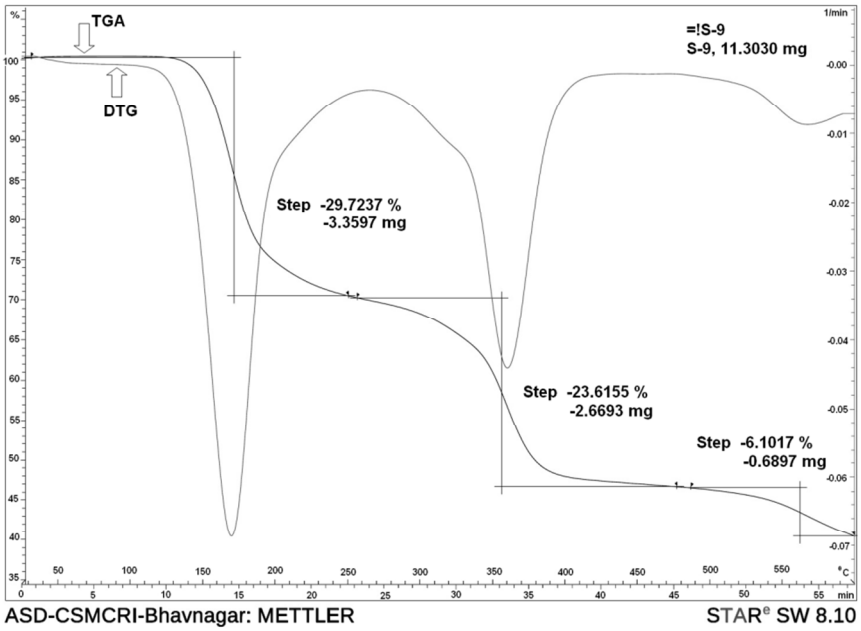


Fig. 6 TG and DTG curve of toluene–3,4–dithiolatoantimony(III) isopropyldithiocarbonate (compound 3).

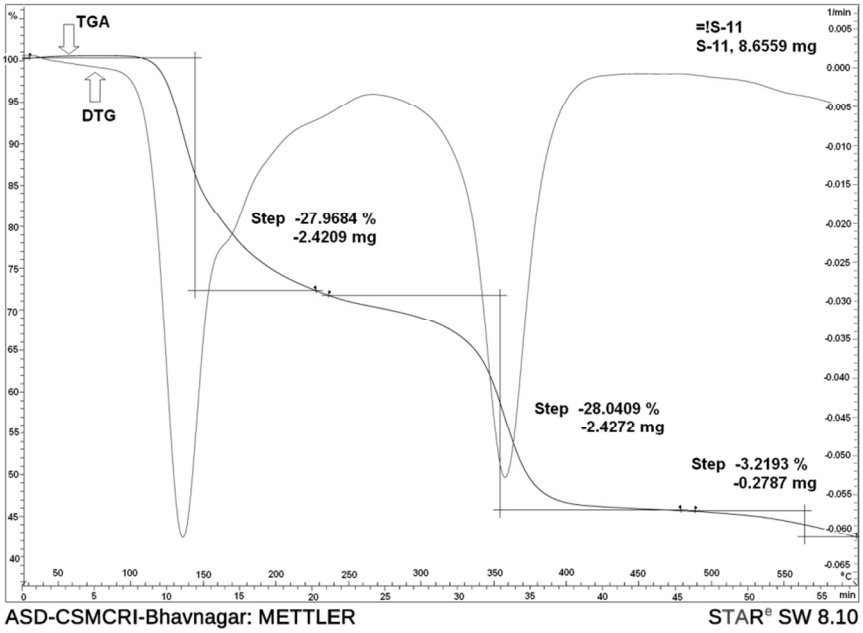


Fig. 7 TG and DTG curve of toluene–3,4–dithiolatoantimony(III) isobutyldithiocarbonate (compound 3).

SEM and EDAX studies of final thermal decomposed product

SEM images of these last thermal decomposed products of compound **1**, **3** and **5** have been shown in Fig. 8 which shows the nano sized rod bundles of large quantity. Its nanorods like morphology confirm the formation of straw like stibnite (antimony sulfide).[33] By electron dispersive X–ray studies, we analyzed the elemental composition of the samples. In all cases (Fig. 9, 10 and 11) of our respected samples, two main peaks are observed for antimony and sulfur atoms in approx 1:1.5 ratios which also support the antimony sulfide species.[33a,34] These studies of final thermal decomposed product proved that the synthesized complexes have capability to form highly pure antimony sulfide at 600°C on their thermal decomposition.

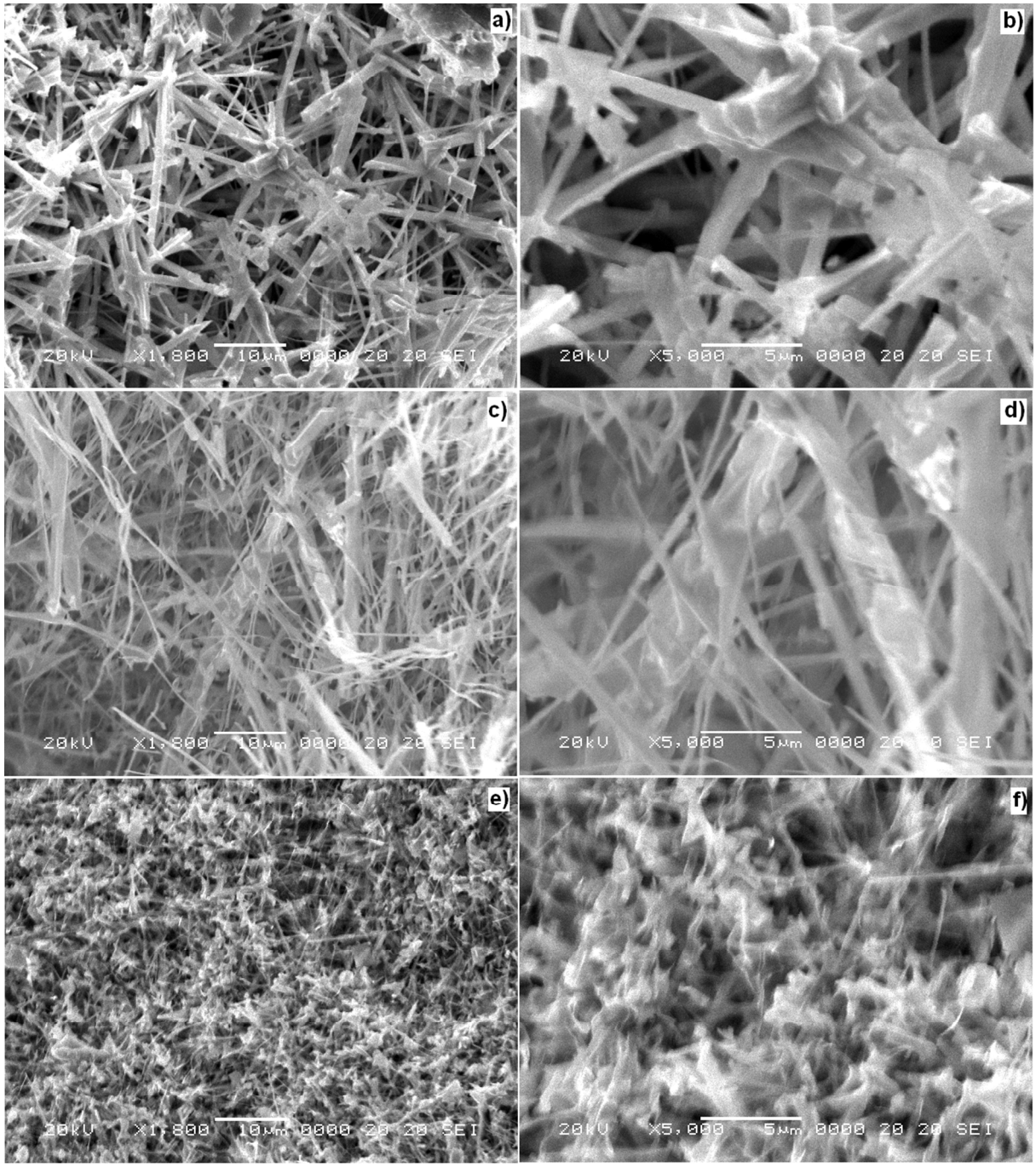


Fig. 8 SEM images of final thermal decomposed product (antimony sulfide) (a) and (b) for Compound 1, (c) and (d) for Compound 3, (e) and (f) for Compound 5.

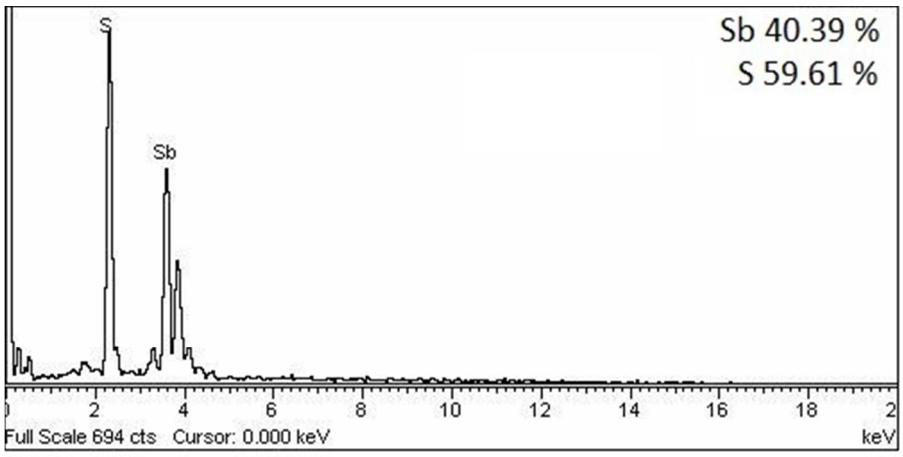


Fig. 9 EDAX spectrum of final thermal decomposed product of compound 1.

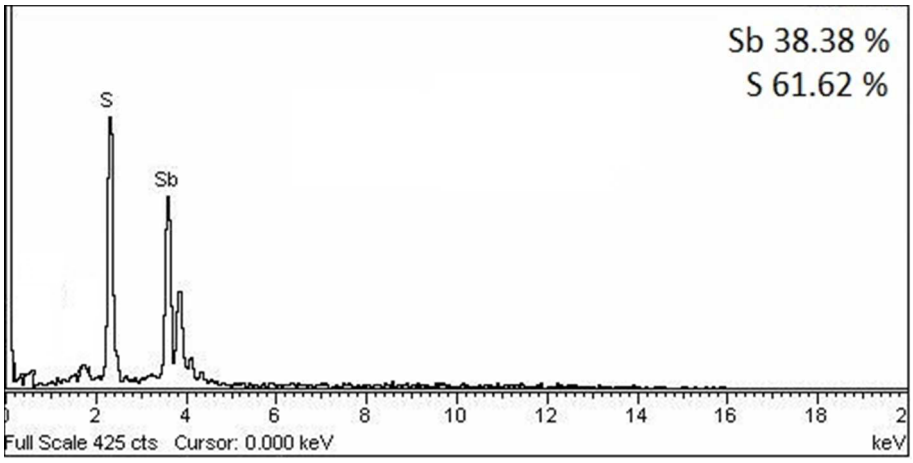


Fig. 10 EDAX spectrum of final thermal decomposed product of compound 3.

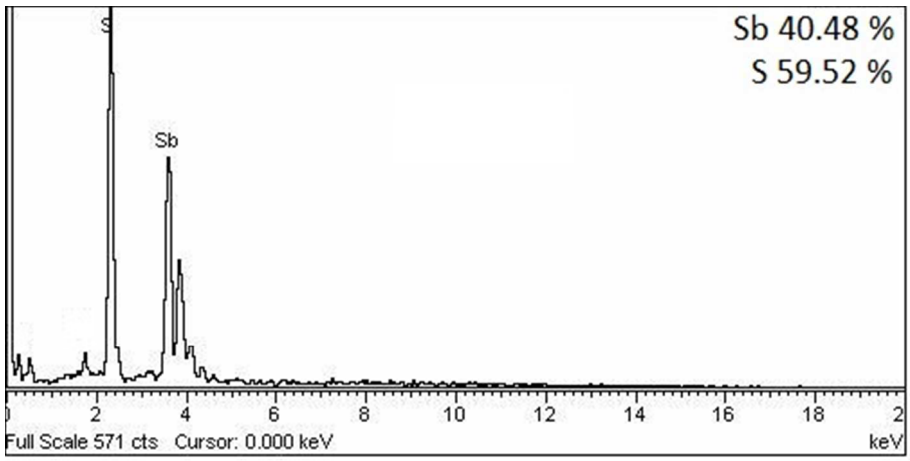


Fig. 11 EDAX spectrum of final thermal decomposed product of compound 5.

ESI – mass studies

Electrospray ionization mass spectra of compound **1** and **3** have been recorded through Waters UPLC–TQD Triple Quadrupole mass spectrometer. ESI is a soft ionization technique in which two important peaks (molecular ion peak and base peak) are observed.[28,35a,b] In the case of these complexes molecular ion peak is either of with very low intensity or do not observed due to pyrolytic decomposition at relatively higher temperature or fragmentation of molecular ion in the ionization chamber.[25,35c] In case of complex **1** molecular ion peak appeared at m/z 382.2 with low intensity (16%) but for complex **3** molecular ion peak do not observed. Whereas base peak for both complexes appeared at the m/z 274.7 which corresponds to the $[CH_3(C_6H_3)S_2Sb]^+$ fragment. This indicate the strong chelating property of the toluene–3,4–dithiol as compared to the alkyldithiocarbonate ligand.

Antimicrobial Studies

The antibacterial and antifungal activities of free ligands and mixed sulfur donor antimony(III) complexes[35d,e] have been tested against four human pathogenic bacterial species (*Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas aeruguinosa*) and two plant fungal species (*Aspergillus niger* and *Penicillium chrysogenum*) at three different concentrations (50, 100 and 200 μg mL^{-1}) shown in Fig. 12, 13 and 14. Their activities have been compared with the standard drugs chloramphenicol (standard antibacterial drug) and terbinafine (standard antifungal drug) and we got nice outcome (Table S4) that the metal to sulfur bonding enhanced the antimicrobial activity as compared to free ligands and standard drug.

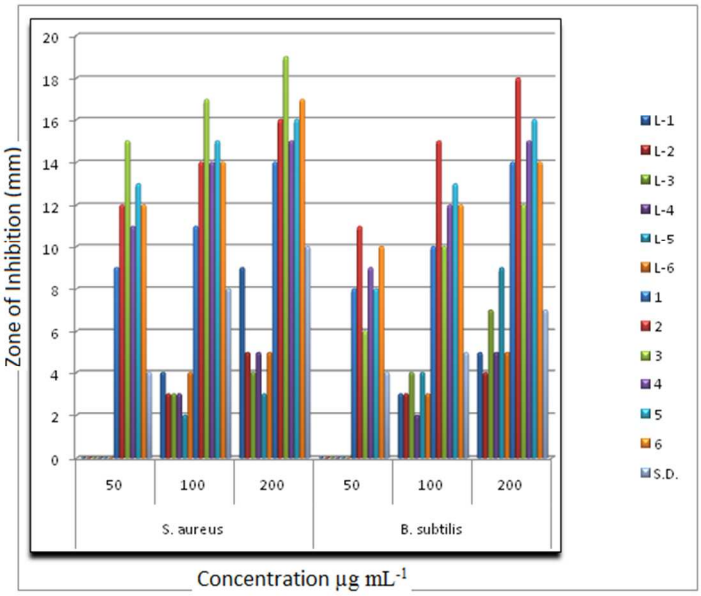


Fig. 12 Antibacterial activities of free ligands and antimony(III) complexes with reference standard drug against gram^{+} bacteria (*S. aureus* and *B. subtillis*).

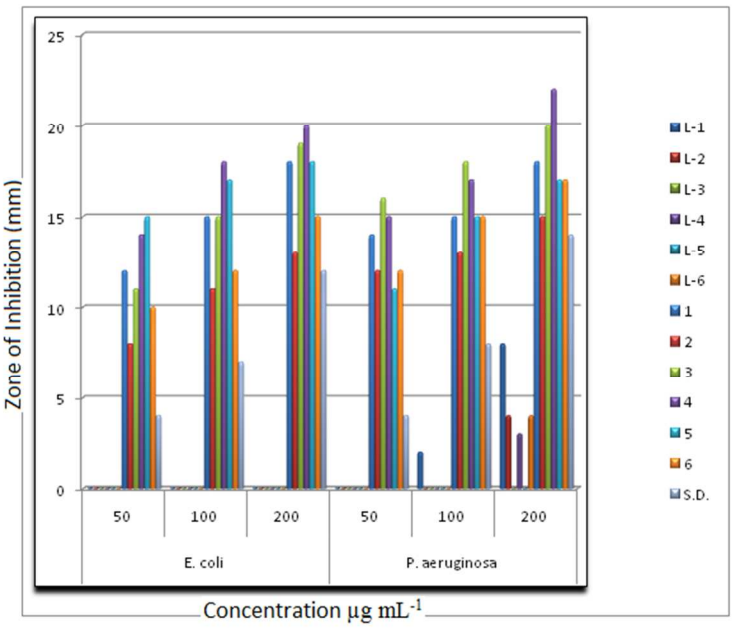


Fig. 13 Antibacterial activities of free ligands and antimony(III) complexes with reference standard drug against gram^{-} bacteria (*E. coli* and *P. aeruginosa*).

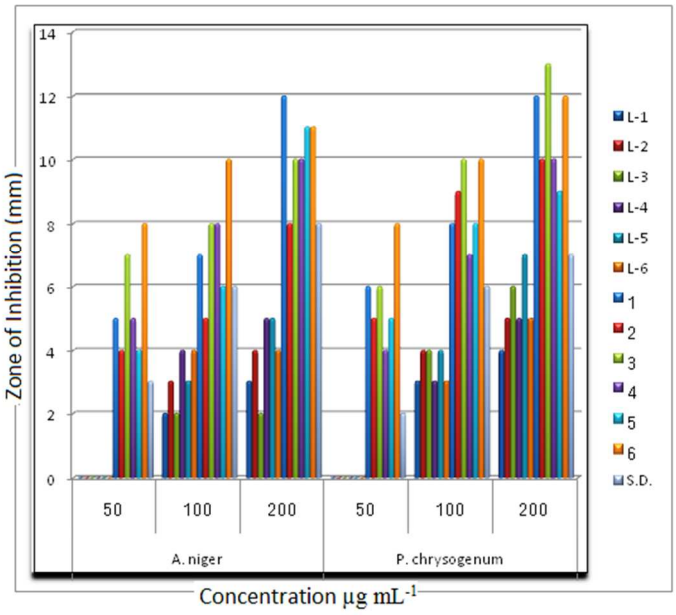


Fig. 14 Antifungal activities of free ligands and antimony(III) complexes with reference standard drug against fungi (*A. niger* and *P. chrysognum*).

By comparing the *in–vitro* antimicrobial activity of the antimony(III) complexes and free ligands with the standard antibiotics, we obtained the following results:

(i) All the complexes have shown greater antibacterial activity than antifungal activity.

(ii) Compound **3** has show the maximum zone of inhibition (22 mm) against *P. aeruginosa* at 200 µg mL^{-1} concentration.

(iii) The synthesized antimony(III) complexes reveals the higher antimicrobial activity than the standard antibiotics and on increasing the concentration activity also increases.

(iv) All compounds have been shown ≤14 mm and ≤15 mm zone of inhibition against the *S. aureus* and *P. aeruginosa* respectively, at 200 µg mL^{-1} concentration.

(v) The $Gram^{-}$ bacteria *E. coli* exhibit greater resistance for Compound **1**, **3**, **4** and **5** at all (50, 100 and 200 µg mL^{-1}) concentrations.

(vi) The antifungal activities of compound **1**, **3** and **5** have been higher than other complexes against *P. chrysogenum* at each concentration.

The above results explain the elevated antimicrobial activity of the mixed sulfur antimony(III) complexes which is due to an incorporation of antimony inside the bacterial and fungal cell membrane. It may be also due to increasing the chelating nature of the ligand to metal which help to penetrate the cell membrane and inhibit the growth of microbes.

Conclusion

On the basis of all the spectral studies, we have analyzed that the toluene–3,4–dithiolatoantimony(III) derivatives of alkyldithiocarbonates adopt the distorted trigonal bipyramidal geometry with the stereochemically active lone pair of electron occupy at the equatorial position. Powder XRD data shows that these complexes are in nanoranged with the lower (monoclinic) symmetry crystal system. On thermal decomposition of these complexes obtained antimony sulfide as a final remaining material in an inert atmosphere which has further confirmed through SEM and EDAX studies. The SEM images show the straw like bundles of nanowires of antimony sulfide and EDAX spectra display the presence of antimony and sulfur elements in 1:1.5 ratios. These antimony(III) complexes with sulfur donor ligands have exhibit greater zone of inhibition against four human pathogenic bacterial (*Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas aeruginosa*) and two plant fungal (*Aspergillus niger* and *Penicilium chrysogenum*) species as compared to the free ligands and standard drugs.

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