APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 404–410
Published online 23 May 2006 in Wiley InterScience
(www.interscience.wiley.com) DOI:10.1002/aoc.1066

Synthetic, spectral, thermal and antimicrobial studies of bis(*N*,*N*-dialkyldithiocarbamato)arsenic(III) and antimony(III) complexes with diphenyldithiophosphate and diphenyldithiophosphinate

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Received 23 January 2006; Revised 6 February 2006; Accepted 16 February 2006

Bis(*N*,*N*-dialkyldithiocarbamato)arsenic(III)/antimony(III) diphenyldithiophosphate/diphenyldithiophosphinate complexes of the type $[R_2NCS_2]_2MS(S)PX_2$ [where M = As and Sb; $NR_2 = N(CH_3)_2$, $N(C_2H_5)_2$ and $N(CH_2)_4$; X = OC_6H_5 and C_6H_5] have been synthesized and characterized by physicochemical, spectral [UV, IR and NMR (^1H, ^{13}C and ^{31}P)] and thermal (TG, DTA and DSC) analysis. The TG analysis shows single-step decomposition of the complex to Sb_2S_3. These complexes have been screened for antibacterial and antifungal activity using the disc diffusion method. All the complexes have shown good activity as antibacterial and antifungal agents, which increased on increasing the concentration. Chloroamphenicol and terbinafin were used as standards for the comparison.

KEYWORDS: arsenic; antimony; TG; DTA; DSC; NMR (^1H, ^{13}C and ^{31}P); antimicrobial

INTRODUCTION

The 1,1-dithiolate ligands, dialkyldithiocarbamates,[1–5] dialkyldithiophosphates,[5–10] diphenyldithiophosphinate[5,9–12] and xanthates,[5,10,13] are versatile in nature and exhibit remarkable diversities in their bonding/coordination possibilities with main group metals and some of them also exhibit biological activities. Dialkyldithiocarbamates have a wide variety of applications such as pesticides (e.g. propineb, zineb, maneb, mancozeb, ziram, thiram), in analytical methods,[14] antiviral agents,[15] antidotes for preventing the effects of phytotoxic agents,[16] antimicrobial agents,[17] antimuscarinic,[18] antiparkinson agents[18] and antitumour drug.[19] In addition, these ligand complexes have important applications in the production of petroleum derivatives, lubricants and polymers, where they are used as accelerators of vulcanization, antioxidants and antihumidity.[20,21]

In continuation of our recent interest on studies on main group metals with sulfur donor organic ligands,[22,23] we report herein some new mixed bis(dialkyldithiocarbamato)antimony(III) complexes with diphenyldithiophosphate and diphenyldithiophosphinate with their spectral, thermal and antimicrobial studies.

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EXPERIMENTAL

Materials and methods

Sodium/ammonium dialkyldithiocarbamates (E. Merck/Fluka) were used as received. Antimony trichloride (E. Merck) was distilled before use. Arsenic trichloride was synthesized[24] and used after distillation. The reactants, such as ammonium diphenyldithiophosphate,[25] sodium diphenyldithiophosphinate[26] and bis(dialkyldithiocarbamato)antimony(III) chloride,[27] were prepared using previously reported methods. Solvents (benzene, acetone, hexane, diethyl ether, alcohols, etc.) were purified and dried by standard methods[28] before use. Melting points were determined in sealed capillary tubes.

Physical measurements

Melting points (only for solid compounds) were determined on a B10 tech India melting point apparatus and are uncorrected. Arsenic and antimony were estimated

iodometrically[29] and sulfur was estimated gravimetrically as barium sulfate.[29,30] Molecular weights were determined cryoscopically in benzene. Elemental analysis (C, H and N) was performed on a Heraeus Carlo Erba 1108 C, H, N analyser at Sophisticated Analytical Instrumentation facility, Punjab University, Chandigarh, India. Infrared spectra were recorded on a Perkin Elmer Model 557 in the range 4000–200 cm^{-1}. The UV spectra were recorded in chloroform solution at room temperature on a Shimadzu UV-1601 UV–visible spectrophotometer within the range 500–200 nm. NMR spectra were recorded in $CDCl_3$ solution on a Jeol AL300 FT-NMR spectrometer, operated at 300.4, 75.45 and 121.5 MHz for ^1H, ^{13}C and ^{31}P, using TMS (tetramethylsilane) and H_3PO_4 as standards, respectively. The TG, DTA and DSC analysis were carried out in an inert atmosphere. For the TG and DTA studies, a Mettler Toledo, model TGA/SDTA 851_e, and for the DSC studies, a Mettler Toledo, model DSC 822_e, were used.

Synthesis of *bis*(dimethyldithiocarbamato) As(III) diphenyldithiophosphate

Bis(*N*,*N*-dimethyldithiocarbamato)arsenic(III) chloride (0.75 g, 2.14 mmol) was dissolved in ~40 ml benzene and solid ammonium diphenyldithiophosphate (0.64 g, 2.14 mmol) was added to it. The contents were refluxed with stirring for ~5 h. The reaction mixture was cooled and the precipitated ammonium chloride was removed by filtration. After removal of solvent, the obtained pale yellow crystalline solid [yield = 1.24 g; 97%; M.P. = 125 °C] was recrystallized in benzene–hexane mixture.

All other bis(dialkyldithiocarbamato)arsenic(III)/antimony(III) diphenyldithiophosphate/diphenyldithiophosphinate were synthesized using similar methods. The pertinent analytical and physico-chemical data for these complexes are summarized in Table 1.

Antimicrobial evaluation

These synthesized complexes and ligands used were screened for their *in vitro* antimicrobial activities against four human pathogenic bacterial species (two Gram-positive and two Gram-negative) [*Staphylococcus aureus* (ATCC 9144), *Bacillus subtilis* (ATCC 6051), *Escherichia coli* (ATCC 9637) and *Pseudomonas aeruginosa* (ATCC 25619)] and two plant fungal species [*Aspergillus niger* (ATCC 9029) and *Penicillium chrysogenum* (ATCC 10106)] using well disc diffusion method.[31] Chloroamphenicol and terbinafin were used as standard drugs for comparison.

The compound was dissolved in DMF, to get 200 μg ml^{-1} concentrated solution. Further progressive double dilutions were performed to obtain the required concentrations of 100 and 50 μg ml^{-1}. Samples of 0.5 ml (containing 10^7 microorganisms per ml) of each investigated microorganisms were added to a sterile nutrient agar (for bacteria)/dextrose agar (for fungi) medium just before solidification, then poured into sterile Petri dishes (9 cm in diameter) and left to solidify. Using a 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 for 24 h for bacteria and at 30 °C for 72 h for fungi, where clear or inhibition zones were detected around each hole. Inhibitory activity was measured (in mm) as the diameter of the inhibition zones. DMF exhibited no effect on the organisms tested.

RESULTS AND DISCUSSION

Syntheses

Mixed *bis*(*N*,*N*-dialkyldithiocarbamato)arsenic(III)/antimony(III) diphenyldithiophosphate and diphenyldithiophosphinate derivatives have been synthesized by the replacement

Table 1. Physico-chemical data of *bis*(dialkyldithiocarbamato)arsenic(III) and antimony(III) diphenyldithiophosphate and diphenyldithiophosphinate

Sample no.	Compound	Yield (%)	M.P. (°C)	Molecular weight, found (calcd)	Analysis (%), found (calcd)				
					C	H	N	S	As/Sb
1	$[(CH_3)_2NCS_2]_2AsS_2P(OPh)_2$	97	125	582 (596.70)	35.98 (36.23)	3.65 (3.71)	4.62 (4.69)	32.18 (32.24)	12.43 (12.55)
2	$[(CH_3)_2NCS_2]_2AsS_2PPh_2$	79	85	551 (564.70)	38.22 (38.28)	3.95 (3.93)	4.91 (4.96)	33.91 (34.07)	13.25 (13.27)
3	$[(C_2H_5)_2NCS_2]_2AsS_2P(OPh)_2$	65	83	647 (652.78)	40.46 (40.48)	4.59 (4.63)	4.24 (4.29)	29.52 (29.47)	11.37 (11.47)
4	$[(C_2H_5)_2NCS_2]_2AsS_2PPh_2$	80	—[a]	608 (620.82)	42.47 (42.56)	4.79 (4.87)	4.46 (4.51)	30.79 (30.99)	11.98 (12.07)
5	$[(CH_3)_2NCS_2]_2SbS_2P(OPh)_2$	82	110	636 (643.49)	33.52 (33.60)	3.41 (3.45)	4.30 (4.35)	29.78 (29.89)	18.86 (18.92)
6	$[(CH_3)_2NCS_2]_2SbS_2PPh_2$	75	147	603 (611.50)	35.24 (35.36)	3.57 (3.63)	3.52 (3.58)	31.26 (31.46)	19.86 (19.91)
7	$[(C_2H_5)_2NCS_2]_2SbS_2P(OPh)_2$	94	117	690 (699.60)	37.69 (37.77)	4.26 (4.32)	3.92 (4.00)	27.38 (27.50)	17.32 (17.40)
8	$[(C_2H_5)_2NCS_2]_2SbS_2PPh_2$	90	—[b]	— (667.50)	39.46 (39.58)	4.48 (4.53)	4.06 (4.19)	28.71 (28.82)	18.18 (18.24)
9	$[(CH_2)_4NCS_2]_2SbS_2P(OPh)_2$	78	—[a]	678 (690.64)	38.24 (38.26)	3.18 (3.21)	3.98 (4.05)	27.72 (27.85)	17.52 (17.59)
10	$[(CH_2)_4NCS_2]_2SbS_2PPh_2$	72	143	648 (663.60)	39.78 (39.82)	3.92 (3.95)	4.16 (4.22)	28.82 (28.99)	18.29 (18.35)

[a] Semi-solid.
[b] Viscous liquid.

DOI: 10.1002/aoc

$$[R_2NCS_2]_2MCl + NH_4S(S)P(OPh)_2 \xrightarrow{\text{Benzene}} [R_2NCS_2]_2MS(S)P(OPh)_2 + NH_4Cl$$

$$[R_2NCS_2]_2MCl + NaS(S)PPh_2 \xrightarrow{\text{Benzene}} [R_2NCS_2]_2MS(S)PPh_2 + NaCl$$

Scheme 1. Reactions of *bis*(*N*,*N*-dialkyldithiocarbamato)arsenic(III)/antimony(III) chloride with ammonium diphenyldithiophosphate/sodium diphenyldithiophosphinate in an equimolar (1 : 1) ratio; M = As and NR_2 = NMe_2, NEt_2; M = Sb and NR_2 = NMe_2, NEt_2, $N(CH_2)_4$.

Table 2. UV and IR spectral data of *bis*(dialkyldithiocarbamato)arsenic(III) and antimony(III) diphenyldithiophosphate and diphenyldithiophosphinate complexes

Compound no.	I	II	III	C–N	C–S	(P)–O–C	P–O–(C)	P–S	P–S	As–S/Sb–S
1	235–275	305	347	1440 (m)	1025 (s)	990 (m)	860 (s)	640 (s)	530 (m)	335 (m)
2	225–270	309	346	1435 (m)	1030 (m)			625 (m)	540 (s)	340 (w)
3	235–278	306	345	1445 (m)	1025 (s)	960 (s)	830 (s)	650 (s)	540 (m)	330 (m)
4	228–275	306	340	1440 (m)	1040 (m)			620 (m)	535 (s)	340 (m)
5	235–275	305	348	1430 (m)	1025 (s)	970 (m)	850 (s)	645 (m)	545 (s)	315 (w)
6	227–280	306	344	1435 (m)	1040 (m)			625 (m)	540 (s)	320 (w)
7	230–280	309	345	1505 (m)	1035 (s)	960 (s)	840 (s)	645 (m)	540 (m)	315 (w)
8	228–280	308	348	1490 (s)	1030 (m)			620 (m)	535 (s)	315 (w)
9	236–277	307	359	1500 (s)	1020 (s)	970 (s)	845 (s)	635 (m)	540 (m)	320 (w)
10	225–270	305	340	1510 (s)	1025 (s)			620 (m)	535 (s)	310 (w)

s = sharp, m = medium and w = weak.

reactions of *bis*(*N*,*N*-dialkyldithiocarbamato)arsenic(III)/antimony(III) chloride with ammonium diphenyldithiophosphate/sodium diphenyldithiophosphinate in an equimolar (1 : 1) ratio in refluxing benzene for ~5 h (Scheme 1). These complexes are either pale yellow solids or semi-solids (except compound **8**, which is a viscous liquid). They are soluble in common organic solvents like benzene, chloroform, acetone, dichloromethane, DMF and DMSO. Their physico-chemical data have been summarized in Table 1.

Electronic spectra

The electronic absorption spectral data of these mixed arsenic(III) and antimony(III) dithiolate complexes are listed in Table 2 and tentative assignments of the important characteristic bands have been made with the help of earlier publications.[10,32,33] The electronic spectra of these newly synthesized complexes exhibit three bands. In all the complexes, the $\pi-\pi^*$ and $n-\pi^*$ transition due to dithiophosphate moieties as well as $\pi-\pi^*$ intramolecular charge transfer transitions due to dithiocarbamate moieties overlap and exhibit more intense broad band between 225 and 280 nm. The second band appears as a shoulder (305–309 nm) and is assigned to $\pi-\pi^*$ transition in the N═C═S (dithiocarbamate) group. The third band of low intensity at 340–359 nm is attributed to $n-\pi^*$ or charge transfer transition due to dithiocarbamate moiety.

Infra-red spectra

The IR spectra of all these complexes have been recorded in the range 4000–200 cm^{-1} and the assignments, made on the basis of previous reports[9,11,22,23,32–35] can be summarized as follows (Table 2).

All these complexes show a single band in the region 1430–1510 cm^{-1} owing to ν(C–N) and another band at 1020–1040 cm^{-1} due to (C–S) stretching vibrations, suggesting the anisobidentate behaviour of the carbamate group in these complexes. The bands of medium to sharp intensity present in the region 960–990 and 830–860 cm^{-1} have been assigned to {(P)–O–C} and {P–O–(C)} stretching vibrations respectively. The bands for ν(P═S) are found in the region 640–650 cm^{-1} (in As complexes) and 635–645 cm^{-1} (in Sb complexes) and, in comparison with spectra of the parent diphenyldithiophosphoric acid, there is a shift towards lower frequencies of 20–45 and 25–50 cm^{-1} in arsenic and antimony complexes, respectively. This shifting indicates most probably anisobidentate chelation of thiophosphoryl sulfur to metal atom. The bands of weak to medium intensities present in the region 530–545, 330–340 and 310–320 cm^{-1} are assigned due to (P–S), (As–S) and (Sb–S) stretching vibrations,[22,23,29] respectively. The (P–S) stretching bands are present in all the complexes at 530–545 cm^{-1}, the corresponding (As–S) and (Sb–S) stretching bands are present in their respective complexes. The diphenyldithiophosphinate complexes show 620–625 and 535–540 cm^{-1} regions and can be assigned to (P═S) and (P═S) stretching modes, respectively.[11,33] The difference between the ν(P═S) (620–625 cm^{-1}) and ν(P–S) (535–540 cm^{-1}; i.e. 85 cm^{-1}) is indicative of anisobidentate coordination of the diphenyldithiophosphinate ligands in these complexes

^{1}H NMR spectral data

All these complexes exhibited the signals due to dialkyldithiocarbamate as well as diphenyldithiophosphate/

DOI: 10.1002/aoc

diphenyldithiophosphinate moieties.[11,22,23,33–36] The dimethyldithiocarbamate derivatives exhibited a singlet at 3.38–3.42 ppm due to methyl protons while diethyldithiocarbamate derivatives exhibited a triplet at 1.24–1.31 ppm and a quartet at 3.73–3.82 ppm due to CH_3 and $-NCH_2$ proton resonances, respectively, and pyrrolidinedithiocarbamate derivatives exhibited two complex patterns at 2.01–2.12 and 3.72–3.78 ppm due to $-CH_2-CH_2-$ and $-NCH_2$ protons, respectively.[22,23] These complexes showed multiplet signals at 7.11–8.05 ppm due to the phenyl ring protons.

^{13}C NMR

The ^{13}C NMR spectra (Table 3) of all these complexes have been recorded in $CDCl_3$ and assignments have been made on the basis of previously reported data.[11,12,22,23,33] The diethyldithiocarbamate derivatives[22,23] exhibited two signals at 12.19–12.28 ppm, 48.46–48.66 ppm due to CH_3 and $-NCH_2$ carbon resonances, respectively, while dimethyldithiocarbamate derivatives showed a signal due to CH_3 carbon resonances at 43.03–43.83 ppm and pyrrolidinedithiocarbamate derivatives exhibited two

Table 3. ^{1}H, ^{13}C and ^{31}P NMR spectral data of *bis*(dialkyldithiocarbamato)arsenic(III) and antimony(III) diphenyldithiophosphate and diphenyldithiophosphinate complexes

Compound	^{1}H NMR chemical shift	^{13}C NMR chemical shift	^{31}P NMR chemical shift
$[(CH_3)_2NCS_2]_2AsS_2P(OPh)_2$	3.38, s, 12H (CH_3 of dtc) 7.12–7.18, m, 10H (Ring protons)	43.03 (CH_3 of dtc) 122.20–129.41 (ring carbons) 197.79 (NCS_2 of dtc)	103.20
$[(CH_3)_2NCS_2]_2AsS_2PPh_2$	3.39, s, 12H (CH_3 of dtc) 7.36–8.05, m, 10H (ring protons)	43.06 (CH_3 of dtc) 127.84–130.71 (ring carbons) 197.94 (NCS_2 of dtc)	59.93
$[(C_2H_5)_2NCS_2]_2AsS_2P(OPh)_2$	1.29, t, 12H (CH_3 of dtc) $J = 7.2$ Hz 3.76, q, 8H (CH_2 of dtc) $J = 7.2$ Hz 7.11–7.39, m, 10H (ring protons)	12.28 (CH_3 of dtc) 48.66 (CH_2 of dtc) 122.18–129.71 (ring carbons) 197.41 (NCS_2 of dtc)	89.79
$[(C_2H_5)_2NCS_2]_2AsS_2PPh_2$	1.26, t, 12H (CH_3 of dtc) $J = 7.1$ Hz 3.79, q, 8H (CH_2 of dtc) $J = 7.1$ Hz 7.27–8.00, m, 10H (ring protons)	12.19 (CH_3 of dtc) 48.46 (CH_2 of dtc) 127.79–139.95 (ring carbons) 197.67 (NCS_2 of dtc)	57.15
$[(CH_3)_2NCS_2]_2SbS_2P(OPh)_2$	3.42, s, 12H (CH_3 of dtc) 7.16–7.39, m, 10H (ring protons)	43.82 (CH_3 of dtc) 122.27–129.23 (ring carbons) 198.6 (NCS_2 of dtc)	89.92
$[(CH_3)_2NCS_2]_2SbS_2PPh_2$	3.41, s, 12H (CH_3 of dtc) 7.26–8.00, m, 10H (ring protons)	43.83 (CH_3 of dtc) 128.07–139.78 (ring carbons) 198.53 (NCS_2 of dtc)	56.91
$[(C_2H_5)_2NCS_2]_2SbS_2P(OPh)_2$	1.28, t, 12H (CH_3 of dtc) $J = 7.2$ Hz 3.77, q, 8H (CH_2 of dtc) $J = 7.2$ Hz 7.11–7.39, m, 10H (ring protons)	12.26 (CH_3 of dtc) 48.64 (CH_2 of dtc) 122.28–129.71 (ring carbons) 197.39 (NCS_2 of dtc)	90.89
$[(C_2H_5)_2NCS_2]_2SbS_2PPh_2$	1.26, t, 12H (CH_3 of dtc) $J = 7.1$ Hz 3.77, q, 8H (CH_2 of dtc) $J = 7.1$ Hz 7.20–7.98, m, 10H (ring protons)	12.25 (CH_3 of dtc) 48.49 (CH_2 of dtc) 127.78–138.95 (ring carbons) 197.67 (NCS_2 of dtc)	57.35
$[(CH_2)_4NCS_2]_2SbS_2P(OPh)_2$	2.10, m, 8H (CH_2 of dtc) 3.74, m, 8H (NCH_2 of dtc) 7.13–7.80, m, 10H (ring protons)	25.83 (CH_2 of dtc) 53.37 (NCH_2 of dtc) 127.78–139.45 (ring carbons) 195.68 (NCS_2 of dtc)	89.89
$[(CH_2)_4NCS_2]_2SbS_2PPh_2$	2.04, m, 8H (CH_2 of dtc) 3.76, m, 8H (NCH_2 of dtc) 7.26–7.99, m, 10H (ring protons)	25.85 (CH_2 of dtc) 53.38 (NCH_2 of dtc) 128.05–139.48 (ring carbons) 194.19 (NCS_2 of dtc)	56.59

s = singlet, t = triplet, q = quartet and m = complex pattern.

DOI: 10.1002/aoc

signals at 25.83–25.85 and 53.37–53.38 ppm due to $-CH_2-CH_2-$ and $-NCH_2$ carbon resonances, respectively. These derivatives also exhibited a very weak singlet at 194.19–198.6 ppm owing to NCS_2 carbon resonances.

In addition, all these complexes[11,12,34] showed signals at 122.18–139.95 ppm for phenyl ring carbon resonances for diphenyldithiophosphate and diphenyldithiophosphinate moieties.

^{31}P NMR spectral data

In all these complexes the diphenyldithiophosphate complexes showed a singlet at 89.79–103.20 ppm. On the basis of the analysis of proton decoupled ^{31}P NMR chemical shift values of a number of metal dialkyl/diphenyldithiophosphates, Glidewell[37] concluded that the complexes showing their ^{31}P NMR signal in the range 82–101 ppm exhibit anisobidentate mode of attachment of the dialkyl/diaryldithiophosphate ligands towards metals. Hence, these diphenyldithiophosphate ligands are behaving as anisobidentate mode of attachment towards metals. In diphenyldithiophosphinate complexes the ^{31}P NMR chemical shift[11] appears at 56.59–59.93 ppm, which also indicates the anisobidentate nature of ligation of the diphenyldithiophosphinate ligand.[12,36]

Antimicrobial activity

The antimicrobial activities[31,38] of all complexes have been assayed at the concentrations 50, 100 and 200 μg ml^{-1} against four bacteria and two fungi. The inhibitory effect of these complexes against bacteria and fungi are given in Table 5. Chloroamphenicol and terbinafin were used as standard drugs for comparison.

The impact of the central metal atom of the compounds was found in the antimicrobial activity against the tested bacterial and fungal species. The results obtained by disc diffusion method indicate that the coordination compounds have enhanced activity compared to the ligands. It indicates that the coordinated As(III) or Sb(III) atom increases the antimicrobial effects. The effect is, as expected, proportional to the concentration of the compounds.

By comparison with the antimicrobial activities of chloroamphenicol (standard antibacterial drug) and terbinafin (standard antifungal drug), the following results have been obtained.

1. All the complexes have higher or equal activity against all organisms than the free ligands.
2. All the dialkyldithiocarbamate ligands possess a pronounced antimicrobial effect against all tested fungi and Gram-positive bacteria and have equal or less activity against Gram-negative bacteria than the antibiotic (chloroamphenicol) used. The free dithiophosphate and phosphinate ligands exhibited less or equal activity against tested microorganisms than the antimicrobials used. It is worth noting that dithiophosphate and phosphinate ligands have no effect against Gram-negative bacteria.
3. All the tested complexes have greater activity than standard antibiotics (chloroamphenicol and terbinafin) against tested fungi and Gram-positive bacteria and have equal or greater activity against Gram-negative bacteria.
4. Compounds **3** and **4** are better antimicrobial agents than chloroamphenicol and terbinafin against all tested organisms.

By comparison of antibacterial activities of these synthesized complexes with some known antibiotics (amikacin, doxycillin, augmentin, sulperazon, unasyn, septrin, cefobid, ampicillin, erythromycin and traivid),[31] we found that these complexes exhibited greater antibacterial effects.

Thermal studies (TG, DTA and DSC)

The mass losses, temperature ranges and final decomposition products for (dialkyldithiocarbamato)antimony(III) diphenyldithiophosphate complexes are presented in Table 4. The results show good agreement with the theoretical formulae as suggested from the analytical data in Table 4. The complexes $[Me_2NCS_2]_2SbS_2P(OC_6H_5)_2$ and

Table 4. Thermal analyses (TG, DTA and DSC) of *bis*(dialkyldithiocarbamato)antimony(III) diphenyldithiophosphate

	TG				DTA[b]		DSC peaks
Step	Temperature[a] range (°C)	Total loss (%)	Loss (%), found (calcd)	Remaining fragments	Temperature (°C)	Type of reaction	Temperature (°C)
I	105–425 A	72.14	72.14 (73.60)	1/2 Sb_2S_3	155 and 240	Endo.	90–161 endo., 166–190 exo., 238 endo., 277–284 exo., 288 exo., >290 endo.
	40–505 B	76.72	76.72 (75.72)	1/2 Sb_2S_3	255	Endo.	117 endo., 121–176 endo., 190–350 mixed endo. and exo.
Weight loss		A	72.14 (73.60)	Remaining material (1/2 Sb_2S_3)			
		B	76.72 (75.72)	A = 27.86 (26.40)			
				B = 23.28 (24.28)			

[a] A = $(Me_2NCS_2)_2SbS_2P(OC_6H_5)$ and B = $(Et_2NCS_2)_2SbS_2P(OC_6H_5)$.
[b] Exo., exothermic process; endo., endothermic process.

DOI: 10.1002/aoc

Table 5. Antibacterial and antifungal activity of free ligands and their bis(*N*,*N*′-dialkyldithiocarbamato)arsenic(III) and antimony(III) diphenyldithiophosphate and diphenyldithiophosphinate complexes

Compound no.	Bacteria (concentration in μg ml^{-1})												Fungi (concentration in μg ml^{-1})					
	S. aureus (G^+)			*B. subtilis* (G^+)			*E. coli* (G^-)			*P. aeruginosa* (G^-)			*A. niger*			*P. chrysogenum*		
	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200
Dtc1	++	+++	+++	++	++	+++	+	++	++	+	++	++	++	+++	+++	++	++	+++
Dtc2	++	+++	+++	++	++	+++	+	++	++	+	++	++	++	+++	+++	++	++	+++
Dtc3	++	+++	+++	++	++	+++	+	++	++	+	++	++	++	+++	+++	++	++	+++
Dtp1	+	++	++	+	+	++	0	0	0	0	0	0	+	+	++	+	+	++
Dtp2	+	+	++	+	++	++	0	0	0	0	0	0	+	+	++	+	++	++
1	++	+++	++++	++	++	+++	+	++	++	+	++	+++	++	+++	++++	+	++	+++
2	++	+++	+++	+	++	+++	+	++	+++	+	++	++	++	+++	++++	+	++	+++
3	++	+++	++++	++	+++	+++	+	++	+++	+	++	+++	++	+++	++++	+	++	+++
4	++	+++	++++	++	+++	++++	+	++	+++	+	++	+++	++	+++	++++	+	++	+++
5	++	+++	++++	+	++	+++	+	++	++	+	++	+++	+	++	+++	++	+++	++++
6	+	++	+++	+	+++	+++	+	++	+++	+	++	++	+	++	+++	+	++	+++
7	++	+++	++++	+	++	+++	+	++	++	+	++	+++	++	+++	++++	++	+++	+++
8	++	+++	+++	+	++	+++	+	++	+++	+	++	++	++	+++	++++	+	++	+++
9	++	+++	++++	+	++	+++	+	++	++	+	++	+++	+	++	+++	++	+++	++++
10	+	++	+++	+	++	+++	+	++	+++	+	++	++	++	+++	++++	+	++	+++
X	+	+	++	+	+	++	+	++	+++	+	++	+++	—	—	—	—	—	—
Y	—	—	—	—	—	—	—	—	—	—	—	—	+	++	++	+	++	++

Well diameter = 6 mm, inhibition zones beyond the holes are: + = 1–5 mm, ++ = 6–10 mm, +++ = 11–15 mm, ++++ = >16 mm and — = not determined, X = Chloroamphenicol and Y = Terbinafin; Dtc1 = $(CH_3)_2NCS_2Na$, Dtc2 = $(C_2H_5)_2NCS_2Na$, Dtc3 = $(CH_2)_4NCS_2NH_4$, Dtp1 = $(C_6H_5O)_2PS_2NH_4$, Dtp2 = $(C_6H_5)_2PS_2Na$.

$[Et_2NCS_2]_2SbS_2P(OC_6H_5)_2$ show only one-stage weight loss in inert atmosphere. These compounds yield antimony(III) sulfide at the end of the first decomposition step due to the decomposition of organic part of the ligands.

In the DTA curves the decomposition of ligands is represented as endothermic peaks at 155 and 240 °C for $[Me_2NCS_2]_2SbS_2P(OC_6H_5)_2$ and at 255 °C for $[Et_2NCS_2]_2SbS_2P(OC_6H_5)_2$. The two-step decomposition of $[Me_2NCS_2]_2SbS_2P(OC_6H_5)_2$ may be due to the carbamate ligand having a smaller alkyl group; therefore, less sterically hindered ligands may form stronger bonds as well as allowing other phosphate ligand to form stronger bonds to decompose in two steps.

The TG result for the complex $[Me_2NCS_2]_2SbS_2P(OC_6H_5)_2$ was confirmed by the DSC curve, which showed an endothermic change of the fusion at 90–161 °C (M.P. = 110 °C), followed by a broad exothermic change at 166–190 °C. Furthermore another endothermic process observed as shown by the peak at 238 °C and exothermic peaks at 277–284 °C and 288 °C. Finally the curve shows a continuous endothermic change above 290 °C.

There is good agreement with DTA and DSC measurements. The DSC curve for $[Et_2NCS_2]_2SbS_2P(OC_6H_5)_2$ complex shows melting at 117 °C, followed by the second process of an endothermic reaction at 121–176 °C. Further endothermic and exothermic changes at 190–350 °C were observed. The presence of more than one endothermic peak in the DSC curve reveals that the pyrolysis occurs in several steps before reaching stable intermediate species.

STRUCTURAL ELUCIDATION

Although it is quite difficult to comment on the molecular structure of these complexes in solid state without actual X-ray crystal structure analysis of at least one of the products, a strong and broad signal in the region 1020–1040 cm^{-1} due to (C═S) stretching vibrations in these derivatives indicate anisobidentate nature of dithiocarbamate ligands. The bands for ν(P═S) appear in the region of 640–650 cm^{-1} [in As(III) complexes] and 635–645 cm^{-1} [in Sb(III) complexes], which are lower by 20–45 cm^{-1} in As(III) and 25–50 cm^{-1} in Sb(III) than that of the parent diphenyldithiophosphoric acid, indicating anisobidentate chelation of dithiophosphate moieties with metal. This is further confirmed by the presence of only one proton-decoupled ^{31}P chemical shift in the range 89.79–103.20 ppm (in diphenyldithiophosphate complexes) and 56.59–59.93 ppm (in diphenyldithiophosphinate complexes). On the basis of the above spectral data it may be concluded tentatively that the ligands are behaving as anisobidentate mode of attachment to the metal in the distorted octahedral complex, where M–S_1, M–S_2 and M–S_3 bonds are

DOI: 10.1002/aoc

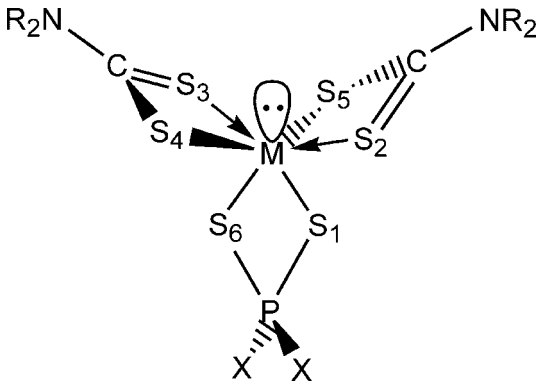

Figure 1. Schematic molecular representation of *bis*(dialkyldithiocarbamato)arsenic(III)/antimony(III) diphenyldithiophosphate/diphenyldithiophosphinate complexes [M = As; $NR_2 = NMe_2$ and NEt_2 and M = Sb; $NR_2 = NMe_2$, NEt_2 and $N(CH_2)_4$ and X = OPh, Ph].

larger than M–S_4, M–S_5 and M–S_6 bonds. The stereochemically active lone pair of electrons occupies the position at the triangular face, formed by S_1, S_2 and S_3 of the distorted octahedra (Fig. 1).

Acknowledgments

We thank Sophisticated Analytical Instrument Facility (SAIF) of Punjab University, Chandigarh, and Central Drug Research Institute (CDRI), Lucknow for providing elemental analysis, IR and NMR spectral data. We thank CSMCRI, Bhavnagar for providing TG, DTA and DSC data. We are also thankful to Microbiology Department of Holkar Science College, Indore for providing the necessary laboratory facilities for antimicrobial studies.

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DOI: 10.1002/aoc