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Synthetic, spectral, thermal and antimicrobial studies on some *bis*(*N*,*N*′-dialkyldithiocarbamato) antimony(III) alkylenedithiophosphates

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***Bis*(*N*, *N*′-dialkyldithiocarbamato)antimony(III) alkylenedithiophosphates of the type $[R_2NCS_2]_2SbS(S)\overline{POGO}$ [where $NR_2 = N(CH_3)_2$, $N(C_2H_5)_2$ and $N(CH_2)_4$; G = $-CH_2-C(C_2H_5)_2-CH_2-$, $-CH_2-C(CH_3)_2-CH_2-$, $-CH(CH_3)-CH(CH_3)-$and $-C(CH_3)_2-C(CH_3)_2-$] were synthesized and characterized by physico-chemical, spectral [UV, IR and NMR (^1H, ^{13}C and ^{31}P)] and thermal (TG, DTA and DSC) analysis. The TG decomposition analysis step of the complex indicated the formation of Sb_2S_3 as the final product. The first endothermic peak in DSC indicated the melting point of the complexes. These complexes were screened for their antimicrobial activities using the disk diffusion method. All the complexes showed good activity as antibacterial and antifungal agents on some selected bacterial and fungal strains, which increased on increasing the concentration. Chloroamphenicol and terbinafin were used as standards for comparison. Copyright © 2007 John Wiley & Sons, Ltd.**

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

INTRODUCTION

The 1,1-dithiolate ligands dialkyldithiocarbamates,[1–5] dialkyldithiophosphates,[5–10] alkylenedithiophosphates[9–11] and alkyldithiocarbonates[5,10,12,13] are versatile in nature and exhibit remarkable diversities in their bonding/coordination patterns with main group metals, and some of them also exhibit biological activities. Dialkyldithiocarbamates have a wide variety of applications such as in pesticides (e.g. propineb, zineb, maneb, mancozeb, ziram and thiram), in analytical methods,[14] as antiviral agents,[15] as antidotes for preventing the effects of phytotoxic agents,[16] as antimicrobial,[17] antimuscarinic[18] and antiparkinson agents[18] and as antitumor drugs.[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 agents.[20,21]

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In continuation of our recent interest in main group metal complexes of sulfur donor organic ligands,[22–26] we report herein the synthetic, spectral, thermal and antimicrobial studies of some mixed *bis*(*N*, *N*′-dialkyldithiocarbamato)antimony (III) alkylenedithiophosphates.

EXPERIMENTAL

Materials and methods

Sodium/ammonium dialkyldithiocarbamates (E. Merck/ Fluka) were used as received. Antimony trichloride (E.Merck) was distilled before use. The reactants, such as ammonium alkylenedithiophosphates[27] and *bis*(*N*, *N*′-dialkyldithiocarbamato)- antimony(III) chloride[28] were prepared by reported methods. Solvents (benzene, acetone, dichloromethane, hexane, diethyl ether, alcohols, etc.) were purified and dried by standard methods[29] before use. Melting points were determined in sealed capillary tubes.

Physical measurements

Melting points (only for solid complexes) were determined on a B10 Tech India melting point apparatus and are uncorrected. Antimony was estimated iodometrically[30] and sulfur

was estimated gravimetrically as barium sulfate.[30,31] Molecular weights were determined cryoscopically in benzene. Elemental analysis (C, H and N) was performed on a Heraeus Carlo Erba 1108 C, H, N analyzer at the 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–vis 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, respectively, using TMS (tetramethylsilane) and H_3PO_4 as standards, respectively. The TG, DTA and DSC analyses were carried out in 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*(*N*, *N*′-diethyldithiocarbamato) Sb(III) neopentylenedithio-phosphate

Bis(*N*, *N*′-diethyldithiocarbamato)antimony(III) chloride (0.56 g; 1.22 mmol), dissolved in ~40 ml benzene, was added to the ammonium 2,2-diethyl propylene- dithiophosphate (0.33 g, 1.22 mmol). The contents were refluxed with stirring for ~5 h. The contents were cooled and precipitated ammonium chloride was removed by filtration. The solvent was stripped off under reduced pressure to obtain a pale yellow crystalline solid, which was recrystallized in benzene–hexane mixture (yield = 0.67 g; 84%; m.p. = 152 °C).

All other complexes were synthesized by adopting similar methods. They were pale yellow crystalline solid or semisolid. The pertinent analytical and physico-chemical data for these complexes are summarized in Table 1.

Microbiological studies

Test microorganisms strains

Strains of four human pathogenic bacterial species [two Gram-positive and two Gram-negative: *Staphylococcus aureus* (ATCC 9144) (G^+), *Bacillus subtilis* (ATCC 6051) (G^+), *Escherichia coli* (ATCC 9637) (G^-) and *Pseudomonas aeruginosa* (ATCC 25 619) (G^-)] and two plant fungal species [*Aspergillus niger* (ATCC 9029) and *Penicillium chrysogenum* (ATCC 10 106)] were screened for their *in vitro* antimicrobial activities.

Method

The compounds were screened for their *in vitro* antimicrobial activities by the well-diffusion method.[32] The compound was dissolved in DMF, to obtain a 200 μg ml^{-1} concentrated solution. Further progressive double dilutions were performed to obtain the required concentrations of 100 and 50 μg ml^{-1}. A 0.5 ml aliquot (containing 10^7 microorganisms ml^{-1}) of the investigated microorganism was 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, when 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.

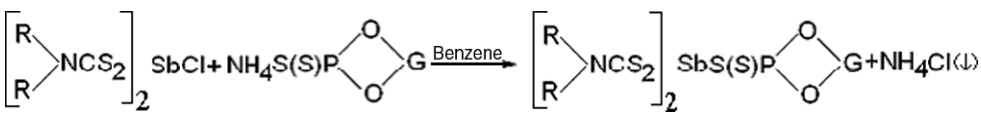
RESULTS AND DISCUSSION

Syntheses

Mixed *bis*(*N*, *N*′-dialkyldithiocarbamato)antimony(III) *O*, *O*′-alkylenedithio-phosphates were synthesized metathetically by the reactions of *bis*(*N*, *N*′-dialkyldithiocarbamato)antimony(III) chloride with ammonium salts of respective *O*, *O*′-alkylenedithiophosphoric acids in an equimolar ratio in refluxing benzene for ~5 h (Scheme 1). These compounds were either pale yellow crystalline solids or semi-solids and were soluble in common organic solvents like benzene, chloroform, acetone, dichloromethane, DMF and DMSO. These compounds along with their physico-chemical data are summarized in Table 1.

Electronic spectra

The electronic absorption spectral data of these mixed *bis*(*N*, *N*′-dialkyldithiocarbamato)antimony(III) alkylenedithiophosphates are listed in Table 2, and tentative assignments of the important characteristic bands were made with the help of earlier publications.[10,26,33] The electronic spectra of these newly synthesized antimony complexes exhibited three bands. In all the antimony complexes, the $\pi-\pi^*$ and $n-\pi^*$ transition are due to dithiophosphate moieties and $\pi-\pi^*$



$NR_2 = N(CH_3)_2$, $N(C_2H_5)_2$ and $N(CH_2)_4$; G=–CH_2–$C(C_2H_5)_2$–CH_2–, –CH_2–$C(CH_3)_2$–CH_2–, –$CH(CH_3)$–$CH(CH_3)$–and –$C(CH_3)_2$–$C(CH_3)_2$.

Scheme 1. Reactions of *bis*(*N*,*N*-dialkyldithiocarbamato)arsenic(III)/antimony(III) chloride with ammonium alkylenedithiophosphate in an equimolar ratio.

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Table 1. Physical and analytical data of *bis*(*N*, *N*′-dialkyldithiocarbamato)antimony(III) alkylenedithiophosphates

Sample no.	Compound	Yield (%)	m.p. (°C)	Molecular weight found (calcd)	Analysis (%) found (calcd)			
					C	H	N	S	Sb
1		89	160	565 (587.46)	26.43 (26.58)	4.38 (4.46)	4.62 (4.77)	32.62 (32.75)	20.54 (20.72)
2		96	165 (d)	546 (559.41)	23.34 (23.62)	3.68 (3.96)	4.92 (5.01)	34.16 (34.39)	21.49 (21.76)
3		65	Semi solid	527 (545.58)	21.86 (22.02)	3.61 (3.70)	5.02 (5.13)	35.07 (35.26)	22.18 (22.32)
4		81	135 (d)	559 (573.44)	24.98 (25.13)	4.16 (4.22)	4.72 (4.88)	33.41 (33.55)	21.14 (21.23)
5		84	152	634 (643.56)	31.68 (31.73)	5.26 (5.32)	4.29 (4.35)	29.77 (29.89)	18.79 (18.92)
6		96	118	604 (615.52)	29.15 (29.27)	4.78 (4.91)	4.44 (4.55)	31.16 (31.25)	19.59 (19.78)

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Table 1. (*Continued*)

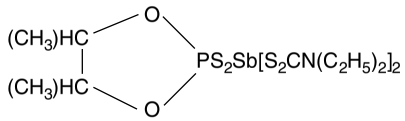
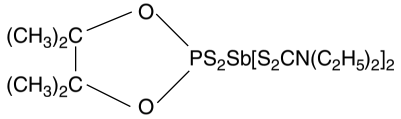
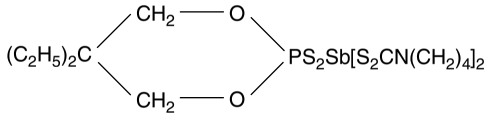
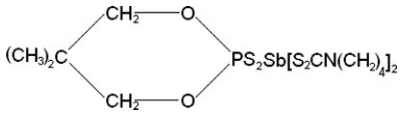
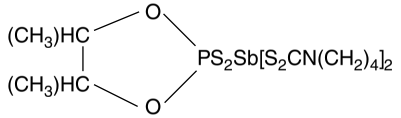
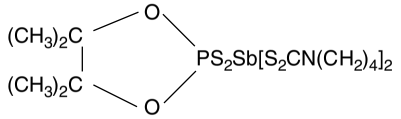
Sample no.	Compound	Yield (%)	m.p. (°C)	Molecular weight found (calcd)	Analysis (%) found (calcd)				
					C	H	N	S	Sb
7		85	Semi solid	580 (601.69)	27.86 (27.95)	4.62 (4.69)	4.59 (4.66)	31.86 (31.97)	20.16 (20.23)
8		85	Semi solid	611 (629.55)	30.39 (30.53)	4.95 (5.12)	4.35 (4.45)	30.99 (31.11)	19.25 (19.34)
9		84	55	618 (639.55)	31.87 (31.93)	4.65 (4.73)	4.32 (4.38)	29.92 (30.08)	18.98 (19.04)
10		93	62	598 (611.51)	29.41 (29.46)	4.23 (4.28)	4.51 (4.58)	31.35 (31.46)	19.87 (19.91)
11		66	72	586 (597.68)	28.05 (28.13)	3.97 (4.05)	4.62 (4.68)	32.07 (32.19)	20.26 (20.33)
12		72	63	612 (625.54)	30.68 (30.72)	4.48 (4.51)	4.42 (4.48)	30.68 (30.75)	19.35 (19.38)

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Table 2. Some relevant UV and IR spectral data of *bis*(*N*, *N*′-dialkyldithiocarbamato)antimony(III) alkylenedithiophosphate complexes

Compound no.	I	II	III	C–N	C–S	(P)–O–C	P–O–(C)	P═S	P–S	Ring vibration	Sb–S
1	238–280	308	347	1500(m)	1015(s)	965(s)	830(s)	635(s)	520(m)	925(s)	320(w)
2	238–280	307	353	1510(s)	1010(m)	970(s)	840(s)	645(s)	510(w)	920(s)	310(w)
3	238–277	306	345	1520(m)	1015(s)	975(s)	835(s)	640(s)	515(m)	910(s)	315(w)
4	230–280	305	356	1515(s)	1025(s)	990(m)	840(s)	650(s)	520(m)	910(s)	320(w)
5	230–275	307	355	1505(m)	1010(s)	965(s)	835(s)	635(s)	520(m)	925(s)	320(w)
6	236–277	308	355	1510(s)	1015(m)	975(s)	840(s)	640(s)	510(w)	920(s)	310(w)
7	230–278	305	348	1515(m)	1010(s)	970(s)	835(s)	645(s)	525(m)	915(s)	315(w)
8	235–283	306	352	1510(s)	1025(s)	985(m)	845(s)	650(s)	520(m)	910(s)	315(w)
9	230–275	310	345	1520(m)	1030(s)	960(s)	830(s)	655(s)	530(m)	920(s)	320(w)
10	236–277	307	359	1510(s)	1025(s)	985(m)	845(s)	640(s)	510(w)	915(s)	310(w)
11	230–282	309	346	1515(s)	1010(s)	980(s)	850(s)	645(s)	515(m)	910(s)	315(w)
12	235–280	308	360	1510(s)	1015(m)	970(s)	840(s)	635(s)	520(m)	930(s)	320(w)

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

intramolecular charge transfer transitions due to dithiocarbamate moieties[26] overlap and exhibit the most intense broad band in the range 230–280 nm. The second band appears as a shoulder (305–309 nm) and is assigned to the $\pi-\pi^*$ transition in the N═C═S (dithiocarbamate) group.[26] The third band of low intensity at 345–359 nm is attributed to $n-\pi^*$ or charge transfer transition due to dithiocarbamate moiety.

Infra-red spectra

The IR spectra of all these complexes were recorded in the range 4000–200 cm^{-1} and the assignments, made on the basis of previous reports[22–28] are summarized in Table 2. All these complexes showed a single band in the region 1500–1520 cm^{-1} due to ν(C–N) and another band at 1010–1030 cm^{-1} due to ν(C C–S), indicating bidentate behavior of the carbamate group in these complexes.[22–24] The bands of medium to sharp intensity present in the region 960–990 and 830–850 cm^{-1} were assigned to {(P) C–O C–C} and {P C–O C–(C)} stretching vibrations, respectively.[27] A sharp band in the region 910–930 cm^{-1} was assigned to the ring vibrations of the dioxaphospholane and dioxaphosphorinane rings.[27,34]

The bands for ν(P C–S) were found in the region 650–685 cm^{-1} and it was observed that, in comparison with spectra of the parent *O*, *O*′-alkylenedithiophosphoric acids, there was a shift of ~35 cm^{-1} towards lower frequency. This shifting indicates most probably a bidentate chelation[33] of thiophosphoryl sulfurs to metal atom. The bands of weak to medium intensities present in the region 510–530 cm^{-1} and 310–320 cm^{-1} were due to (P C–S) and (Sb C–S) stretching vibrations[30], respectively.

^{1}H NMR spectral data

^{1}H NMR spectra of *bis*(*N*, *N*′-dialkyldithiocarbamato)antimony(III) complexes with *O*, *O*′-alkylenedithiophosphate showed the characteristic proton resonances for the corresponding *N*, *N*′-dialkyldithiocarbamate[22–26,28,33] as well as *O*, *O*′-alkylenedithiophosphate[27,30] proton moieties. The dimethyldithiocarbamate complexes showed a singlet at 3.42–3.44 ppm due to NCH_3 proton resonances while diethyldithiocarbamate complexes showed a multiplet at 1.06–1.47 due to overlapping of CH_3 protons of carbamate with CH_3 protons of dithiophosphate (complex **5** showed a triplet at 1.31 ppm) and a quartet at 3.80–3.84 ppm due to NCH_2 proton resonances. The pyrrolidinedithiocarbamate complexes showed two multiplets at 2.05–2.13 and 3.73–3.84 ppm due to CH_2 and NCH_2 proton resonances, respectively. The appearance of a doublet in the six-membered ring (dioxaphosphorinane ring) and a multiplet in the five-membered ring (dioxaphospholane ring) dithiophosphate complexes was due to the coupling of OCH_2 and OCH protons with ^{31}P nuclei, respectively (Table 3).

^{13}C NMR

The proton-decoupled ^{13}C NMR spectra (Table 3) of all these complexes were recorded in $CDCl_3$ and assignments were made on the basis of previously reported data.[22–28,33,35–37] These complexes showed characteristic resonances due to *N*, *N*′-dialkyldithiocarbamate and *O*, *O*′-alkylenedithiophosphate moieties and showed good agreement with previously reported data. The ^{13}C NMR spectral data of the dimethyldithiocarbamate derivatives showed a signal in the range 43.28–43.87 ppm due to methyl carbon. The complexes of diethyldithiocarbamate showed two signals, one at 11.76–12.29 ppm and other at 48.04–48.64 ppm due to CH_3 and NCH_2 carbons, respectively. The pyrrolidinedithiocarbamate complexes showed two signals at 25.86–25.89 and 53.42–53.44 ppm due to CH_2 and NCH_2 carbons, respectively. All these complexes showed a weak signal at 197.16–200.28 ppm due to NCS_2 carbon resonances.

The very weak signals were also observed for quaternary carbons in a six-member ring and for OCH (at 74.75–79.28 ppm) in $OCMe_2$ (86.21–89.59 ppm) carbons

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Table 3. ^{1}H, ^{13}C and ^{31}P NMR spectral data for *bis*(*N*, *N*′-dialkyldithiocarbamato)antimony(III) alkylenedithiophosphate complexes

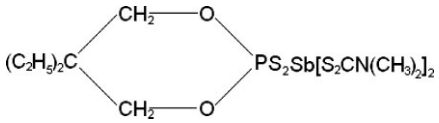
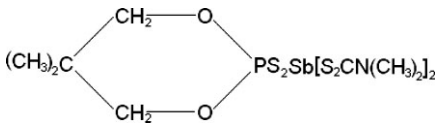
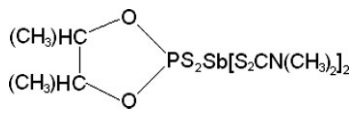
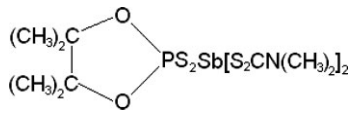
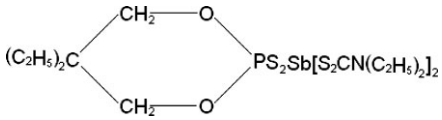
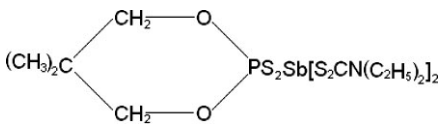
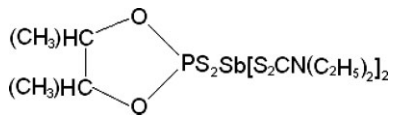
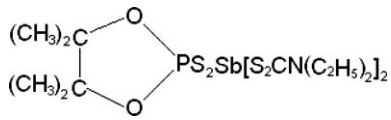
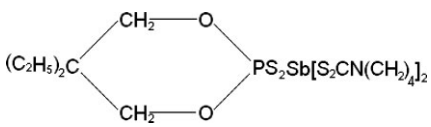
Compound	^{1}H Chemical shifts (ppm)	^{13}C Chemical shifts (ppm)	^{31}P Chemical shifts (free acid)
	0.85, t, 6H (CH_3 of dtp) $J = 7.6$ Hz 1.47, q, 4H (CH_2 of dtp) $J = 7.6$ Hz 3.44, s, 12H (NCH_3 of dtc) 4.14, d, 4H (OCH_2 of dtp) $J = 15.8$ Hz	7.20 (CH_3 of dtp) 23.15 (CH_2 of dtp) 36.66 (q C of dtp) 43.86 (NCH_3 of dtc) 72.90 (OCH_2 of dtp) 200.28 (NCS_2 of dtc)	93.85 (77.80)
	1.06, s, 6H (CH_3 of dtp) 3.42, s, 12H (NCH_3 of dtc) 4.08, d, 4H (OCH_2 of dtp) $J = 15.9$ Hz	21.92 (CH_3 of dtp) 32.68 (q C of dtp) 43.87 (NCH_3 of dtc) 75.81 (OCH_2 of dtp) 200.16 (NCS_2 of dtc)	95.49 (78.58)
	1.35, d, 6H (CH_3 of dtp) $J = 6.0$ Hz 3.47, s, 12H (NCH_3 of dtc) 4.25–4.45, m, 2H (OCH of dtp)	15.60 (CH_3 of dtp) 43.28 (NCH_3 of dtc) 79.06 (OCH of dtp) 200.08 (NCS_2 of dtc)	113.07 (95.46)
	1.38, s, 12H (CH_3 of dtp) 3.42, s, 12H (NCH_3 of dtc)	24.48 (CH_3 of dtp) 43.83 (NCH_3 of dtc) 89.59 (OC of dtp) 198.68 (NCS_2 of dtc)	109.08 (93.07)
	0.85, t, 6H (CH_3 of dtp) $J = 7.5$ Hz 1.31, t, 12H (CH_3 of dtc) $J = 7.2$ Hz 1.47, q, 4H (CH_2 of dtp) $J = 7.5$ Hz 3.81, q, 8H (NCH_2 of dtc) $J = 7.2$ Hz 4.14, d, 4H (CH_2O of dtc) $J = 15.8$ Hz	7.12 (CH_3 of dtp) 12.25 (CH_3 of dtc) 23.10 (CH_2 of dtp) 37.39 (q C of dtp) 48.64 (CH_2 of dtc) 72.74, d, (OCH_2 of dtp) $J = 7.8$ Hz 197.46 (NCS_2 of dtc)	98.05 (77.80)
	1.06–1.47, m, 18H (CH_3 of dtp and dtc) 3.80, q, 4H (NCH_2 of dtc) $J = 7.2$ Hz 4.07, d, 4H (OCH_2 of dtp) $J = 15.5$ Hz	12.19 (CH_3 of dtc) 21.82 (CH_3 of dtp) 32.49 (q C of dtp) 48.62 (CH_2 of dtc) 75.40, d, (OCH_2 of dtp) $J = 6.7$ Hz 197.16 (NCS_2 of dtc)	98.84 (78.58)
	1.17–1.33, m, 18H (CH_3 of dtp and dtc) 3.80, q, 4H (NCH_2 of dtc) $J = 7.1$ Hz 4.46–4.62, m, 2H (OCH of dtp)	11.76 (CH_3 of dtc) 15.19 (CH_3 of dtp) 48.04 (CH_2 of dtc) 74.75 (OCH of dtp) 197.32 (NCS_2 of dtc)	111.51 (95.49)
	1.23–1.47, m, 24H (CH_3 of dtc and dtp) 3.84, q, 8H (NCH_2 of dtc) $J = 7.1$ Hz	12.29 (CH_3 of dtc) 24.49 (CH_3 of dtp) 48.49 (CH_2 of dtc) 86.21 (OC of dtp) 198.37 (NCS_2 of dtc)	110.18 (93.07)
	0.83, t, 6H (CH_3 of dtp) $J = 7.5$ Hz 1.46, q, 4H (CH_2 of dtp) $J = 7.5$ Hz 2.06–2.11, m, 4H (CH_2 of dtc) 3.76–3.84, m, 4H (NCH_2 of dtc)	7.17 (CH_3 of dtp) 23.10 (CH_2 of dtp) 25.86 (CH_2 of dtc) 37.46 (q C of dtp)	96.68 (77.80)

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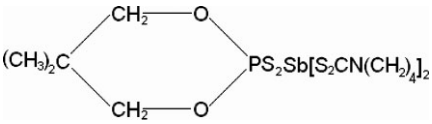
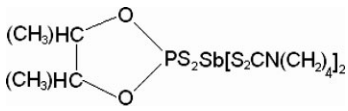
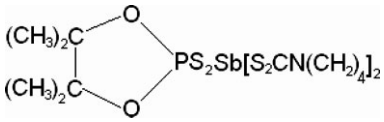
Table 3. (*Continued*)

Compound	^{1}H Chemical shifts (ppm)	^{13}C Chemical shifts (ppm)	^{31}P Chemical shifts (free acid)
	4.13, d, 4H (OCH_2 of dtp) J = 15.6 Hz	53.43 (NCH_2 of dtc) 73.06, d, (OCH_2 of dtp) J = 7.4 Hz 198.76 (NCS_2 of dtc)	
	1.06, s, 6H (CH_3 of dtp) 2.05–2.10, m, 8H (CH_2 of dtc) 3.76–3.80, m, 8H (NCH_2 of dtc) 4.08, d, 4H (OCH_2 of dtp) J = 15.6 Hz	21.92 (CH_3 of dtp) 25.89 (CH_2 of dtc) 32.52 (q C of dtp) 53.44 (NCH_2 of dtc) 75.79, d, (OCH_2 of dtp) J = 8.1 Hz 198.6 (NCS_2 of dtc)	98.74 (78.58)
	1.34, d, 6H (CH_3 of dtp) J = 7.0 Hz 2.08–2.13, m, 4H (CH_2 of dtc) 3.73–3.77, m, 4H (NCH_2 of dtc) 4.46–4.51, m, 2H (OCH of dtp)	15.74 (CH_3 of dtp) 25.88 (CH_2 of dtc) 53.42 (NCH_2 of dtc) 79.28 (OCH of dtp) 198.9 (NCS_2 of dtc)	112.65 (95.49)
	1.38, s, 12H (CH_3 of dtp) 2.07–2.12, m, 8H (CH_2 of dtc) 3.75–3.80, m, 8H (NCH_2 of dtc)	23.98 (CH_3 of dtp) 25.89 (CH_2 of dtc) 53.42 (NCH_2 of dtc) 87.09 (OC of dtp) 197.8 (NCS_2 of dtc)	115.82 (93.07)

s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, six = sextet, q C = quaternary carbon, dtc = dialkyldithiocarbamate and dtp = alkylenedithiophosphate.

resonances.[23–25] The six-membered ring complexes OCH_2 carbon resonances appeared as doublets due to coupling with phosphorous nuclei.

^{31}P NMR

The ^{31}P NMR chemical shift values (Table 3) appear to be dependent on the size of heterocyclic rings. In the spectra of these synthesized derivatives, the ^{31}P NMR signal showed downfield shifting of about 19–31 ppm in the corresponding dioxaphosphorinane (six-membered ring) and 7–18 ppm in the corresponding dioxaphospholane (five-membered ring) with respect to their parent alkylenedithiophosphoric acids[27] [77.80–78.58 ppm for dioxaphosphorinane (for six-membered rings) and 93.07–95.49 ppm for dioxaphospholane (for five membered rings)], indicating the bidentate mode of attachment of alkylenedithiophosphate ligands. These results are in conformity with the conclusion from IR spectra about the bidentate mode of bonding of the alkylenedithiophosphate ligands in these derivatives.

STRUCTURAL ELUCIDATION

In IR spectra of all these antimony complexes, the presence of a strong and broad signal in the region 1500–1520 cm^{-1} due to ν(C C–N) and 1010–1030 cm^{-1} due to ν(C═S) indicates the anisobidentate nature of dithiocarbamate ligands. A band due to ν(P═S) at 650–685 cm^{-1} was observed to be shifted by ~35 cm^{-1} towards lower frequency in comparison to the parent alkylenedithiophosphoric acids, indicating anisobidentate chelation of these moieties with antimony, which was further confirmed by the presence of only one proton-decoupled ^{31}P chemical shift in the range 96.68–109.69 δ ppm (in dioxaphosphorinane) and 102.65–113.07 δ ppm (in dioxaphospholane) complexes, respectively. The IR [ν(C C–N), ν(C═S) and ν(P═S)] and ^{31}P NMR data indicate that these complexes have similar molecular structure to *bis*(*N*,*N*-dialkyldithiocarbamato)Sb(III) diphenyldithiophosphate.[26] Hence, distorted octahedral geometry, with a stereochemically active lone pair of electrons occupying one of the triangular face of the octahedra has been tentatively proposed for these complexes (Fig. 1).

Thermal studies (TG, DTA and DSC)

The mass losses, temperature ranges and final decomposition products for (*N*, *N*′-dialkyldithiocarbamato)antimony(III) alkylenedithiophosphate complexes are presented in Table 4. The results show good agreement with the theoretical formulae as suggested from the analytical data, Table 1.

The complexes $[(CH_3)_2NCS_2]_2SbS_2\overline{POCH_2CMe_2CH_2O}$ and $[(C_2H_5)_2NCS_2]_2SbS_2\overline{POCH_2CMe_2CH_2O}$ showed single- and

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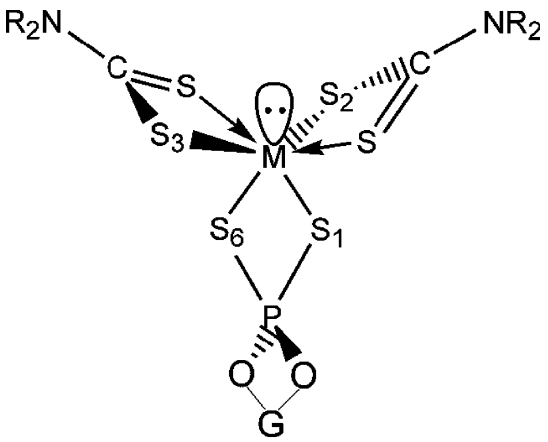

NR_2 = $N(CH_3)_2$, $N(C_2H_5)_2$ and $N(CH_2)_4$ and G= $-CH_2-C(CH_2CH_3)_2CH_2-$, $-CH_2-C(CH_3)_2CH_2-$,$-CH(CH_3)CH(CH_3)-$and $-C(CH_3)_2C(CH_3)_2-$.

Figure 1. Schematic molecular representation of *bis* (*N*, *N*′-dialkyldithiocarbamato)antimony(III) alkylenedithiophosphate.

double-stage weight loss in inert atmosphere, respectively. These compounds yielded highly pure antimony(III) sulfide at the end of the decomposition steps due to the decomposition of the organic part of the ligands. The low-temperature decomposition and non-horizontal line[38] in the TG curve indicates the instability of the complexes.

In the DTA curves decomposition of ligands is represented as endothermic peaks at 225 and 265 °C (for $[Me_2NCS_2]_2SbS_2\overline{POCH_2CMe_2CH_2O}$) and at 240 and 330 °C (for $[Et_2NCS_2]_2SbS_2POCH_2CMe_2CH_2O$).

The DSC of $Me_2NCS_2]_2SbS_2\overline{POCH_2CMe_2CH_2O}$ showed good agreement and an endothermic change at 165 °C, which is also the melting point of the complex. Another endothermic change at 202 °C was observed followed by exothermic change at 208 °C. After this, mixed endothermic and exothermic changes were observed up to 229 °C. Another endothermic change at 235 °C followed by an exothermic change at 237 °C and an endothermic change at 239 °C were observed. The broad exothermic changes were also observed above 240 °C.

The DSC of $[Et_2NCS_2]_2SbS_2\overline{POCH_2CMe_2CH_2O}$ showed that the complex melts at 119 °C. The second endothermic peak was observed at 178 °C, followed by broad endothermic changes at 182–208 °C. Finally the complex showed mixed exothermic and endothermic changes above 208 °C.

Antimicrobial activity

The antimicrobial activities[32,38] of all complexes were assayed at the concentrations 50, 100 and 200 μg ml^{-1} against four bacterial and two fungal species. The inhibitory effects 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 the disk diffusion method indicated that the coordination compounds have enhanced activity compared with the ligands. This indicates that the coordinated 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 less or equal activity against Gram-negative bacteria than the antibiotic (chloroamphenicol) used. The free alkylenedithiophosphate ligands exhibited less or equal activity against

Table 4. Thermal analyses (TG, DTA and DSC) of *bis*(*N*, *N*′-dialkyldithiocarbamato)antimony(III) alklenedithiophosphates

	TG				DTA[a]		
Step	Temperature range (°C)[a]	Total loss (%)	Different loss (%), found (calcd)	Remaining fragments	Temperature (°C)	Type of reaction	DSC Peaks Temperature (°C)
I	125–590 A	69.89	69.89 (69.63)	1/2 Sb_2S_3	245	End.	119 End., 178 End., 182–208 Exo.
	100–370 B	65.12	65.12 (65.09)	1/2 (Sb_2S_3 + NCS_2)	240	End.	165 End., 202 End., 208 End., 229 End.–Exo.,
II	370–590 B	71.91	71.91 (72.39)	1/2 Sb_2S_3	335	Endo.	235 Endo., 237 Exo., 239 Exo., >240 Exo.
Total loss, %A = 69.89			69.89 (69.63)	Remaining material (1/2 Sb_2S_3)			
Total loss, %B = 71.91			71.91 (72.39)	A = 30.10 (30.37)			
				B = 28.09 (27.61)			

[a] A = $[Et_2NCS_2]_2SbS_2\overline{POCH_2CMe_2CH_2O}$ and B = $[Me_2NCS_2]_2SbS_2\overline{POCH_2CMe_2CH_2O}$.
[b] End.: endothermic process; Exo.: exothermic process.

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

	Zone of inhibition (in mm) by taking known concentration of complexes																	
	Bacteria (concentration in μg ml^{-1})												Fungi (concentration in μg ml^{-1})					
	S. aureus (G^+)			*B. subtilis* (G^+)			*E. coli* (G^-)			*P. aeruguinosa* (G^-)			*A. niger*			*P. chrysogenum*		
Compound	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200
Dtc1	8	11	13	8	9	12	3	6	8	4	6	8	7	11	14	6	8	11
Dtc2	8	11	14	7	9	13	4	6	9	4	6	8	6	11	13	6	9	12
Dtc3	7	11	13	7	9	13	3	7	9	2	8	9	8	11	13	7	9	13
Dtp 1	3	6	9	2	4	7	0	0	0	0	0	0	2	4	7	2	5	8
Dtp 2	2	4	7	2	7	9	0	0	0	0	0	0	2	4	8	2	7	9
Dtp 3	2	3	5	2	4	8	0	0	0	0	0	0	2	4	6	2	3	5
Dtp 4	2	3	5	1	3	5	0	0	0	0	0	0	1	3	4	1	2	4
1	4	8	14	6	11	15	2	7	10	3	8	15	2	7	14	7	11	14
2	3	8	15	3	8	15	4	8	15	4	9	14	8	14	20	5	9	15
3	4	9	14	5	7	14	4	9	14	5	9	15	8	12	15	3	7	13
4	5	9	15	4	9	14	5	8	15	4	8	10	8	11	15	8	13	15
5	4	8	14	5	9	15	4	6	10	4	7	13	7	12	18	8	12	19
6	8	12	19	9	12	15	4	7	13	3	6	13	9	13	18	5	9	14
7	7	13	19	4	9	14	5	9	15	5	10	15	4	9	14	8	14	19
8	4	9	14	7	11	15	5	9	15	4	6	10	6	14	19	6	11	15
9	6	12	15	4	7	14	5	8	10	4	7	10	9	13	19	8	15	20
10	4	8	15	4	6	10	4	6	9	4	9	15	7	11	15	4	9	14
11	8	13	19	5	8	14	5	7	10	5	9	14	7	12	19	4	9	13
12	8	11	15	4	6	10	4	7	12	2	6	10	2	7	12	6	11	15
X	3	5	7	2	4	8	3	7	11	2	6	11	Nd	Nd	Nd	Nd	Nd	Nd
Y	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	3	7	9	3	6	9

Nd = not detetected, X = chloroamphenicol and Y = terbinafin; Dtc1 = $(CH_3)_2NCS_2Na$, Dtc2 = $(C_2H_5)_2NCS_2Na$, Dtc3 = $(CH_2)_4NCS_2NH_4$, Dtp1 = $OCH_2C(C_2H_5)_2CH_2OPS_2NH_4$, Dtp2 = $OCH_2C(CH_3)_2CH_2OPS_2NH_4$, Dtp3 = $OCH(CH_3)CH(CH_3)OPS_2NH_4$, Dtp4 = $OC(CH_3)_2C(CH_3)_2OPS_2NH_4$.

tested microorganisms than the antimicrobials used. It is worth noting that alkylenedithiophosphates 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 **2, 6** and **7** are better antimicrobial agents than chloroamphenicol and terbinafin against all tested microorganisms.

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.

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