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Synthetic, spectroscopic and antimicrobial studies of bis(dialkyldithiocarbamato)diorganodithiophosphato-bismuth(III) complexes

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Some mixed sulfur ligand complexes of bismuth(III) have been synthesized by the reactions of bis(dialkyldithiocarbamato)bismuth(III) chloride with sodium/ammonium diorganodithiophosphates in equimolar ratio in anhydrous benzene there will be a yield of: bis(dialkyldithiocarbamato)diorganodithiophosphatobismuth(III) of the type $[(R'_2NCS_2)_2BiS_2P(OR)_2]$, where R' = Me and Et and R = Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu and Ph. These newly synthesized complexes have been characterized by elemental (C, H, N, S and Bi) analysis, molecular weight determination and spectral [UV, IR and NMR (^{1}H, ^{13}C and ^{31}P)] studies. The free ligand and its mixed metal complexes were tested *in vitro* against a number of microorganisms to assess their antimicrobial properties. The results are indeed positive. In addition to these studies, the complexes also show good antibacterial effect over some of the previously investigated antibiotics. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: fungicides; bactericides; bismuth(III) complexes; 1,1-dithiolates; IR; NMR (^{1}H, ^{13}C and ^{31}P)

INTRODUCTION

The 1,1-dithiolate ligands (dialkyldithiocarbamates,[1,2] dialkyldithiophosphates[3–7] and xanthates[7,8]) are versatile in nature and exhibit remarkable diversities in their bonding/coordination possibilities (Fig. 1) with main group metals, some of them also exhibiting biological activities. Dialkyldithiocarbamates have a wide variety of applications, such as pesticides (e.g. propineb, zineb, maneb, mancozeb, ziram, thiram) and in analytical methods.[9,10] Other current uses are as antiviral agents,[11] antidotes for preventing the effects of phytotoxic agents,[12] bactericides and antimicrobial agents,[13] antitumour drugs,[14] antioxidants and antihumidity agents.[15,16]

Although a number of tris as well as mixed-halide 1,1-dithiolates of bismuth(III) and organobismuth(III) derivatives with these ligands have been isolated and several of them have been characterized fully by X-ray diffraction methods,[6–8,15,17] the corresponding bismuth(III) derivatives with mixed 1,1-dithiolate ligands do not appear to have received much attention by the chemists.[18,19] In continuation of our recent interest in synthetic and structural aspects of mixed-sulfur ligand complexes of main group metals,[18–23] we report herein the results of the syntheses, spectroscopic characterization and antimicrobial activity studies of the some new mixed-sulfur ligand compounds of bismuth(III) of the type $[(R'_2NCS_2)_2BiS_2P(OR)_2]$ (where R' = Me and Et; R = Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu and Ph).

EXPERIMENTAL

Materials

Bismuth trichloride (Fluka) was purified by sublimation before use. Sodium dialkyldithiocarbamates (Merck) was used as received. The reactants, such as diorganodithiophosphoric acids and their sodium/ammonium salts[6,7] and bis(dialkyldithiocarbamato)bismuth(III) chloride,[24] were prepared by the earlier reported methods. Solvents (benzene, acetone, hexane, diethyl ether and alcohols) were purified and dried by standard methods[25] before use.

Analytical methods and physical measurements

Bismuth was determined complexometrically by titration against standard EDTA solution using xylenol orange as an indicator, and sulfur was determined gravimetrically

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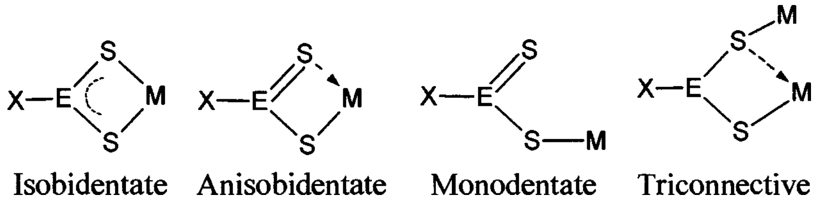

Figure 1. Structural possibilities for the 1,1-dithiolate ligands [where E = C, X = NR_2, E = P, X = $(OR)_2$].

as barium sulfate.[26] Melting points were determined in sealed capillary tubes. Molecular weights were determined cryoscopically in benzene.

The 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. Infrared spectra were recorded on a Perkin Elmer Model 557 FTIR spectrophotometer in the range 4000–200 cm^{-1}. The electronic spectra were recorded in chloroform solution at room temperature on a Shimadzu UV-1610 UV–visible spectrophotometer in the range 200–500 nm. Elemental analyses (C, H and N) were performed on a Heraeus Carlo Erba 1108 C, H, N analyser.

Antimicrobial studies

The following strains of bacteria and fungi were used: *Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa, Salmonella typhi, Aspergillus niger* and *Penicillium chrysogenum*. Antimicrobial activities were evaluated by means of the agar diffusion method[27,28] for the tested compounds as follows.

A 0.5-ml spore suspension (10^6–10^7 spore ml^{-1}) of each of the investigated organisms was added to a sterile agar medium just before solidification and 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 the tested compounds dissolved in DMF (50 ppm, 100 ppm and 200 ppm) were 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.

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

Syntheses of bismuth(III) complexes

Bismuth(III) complexes of the general formula $[(R'_2NCS_2)_2BiS_2P(OR)_2]$ (where R′ = Me and Et; R = Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu and Ph) were prepared by the reaction of bis(dialkyldithiocarbamato)bismuth(III) chloride with sodium/ammonium diorganodithiophosphate in the molar ratio 1 : 1. The details of syntheses are as follows:

A mixture of bis(dimethyldithiocarbamato)bismuth(III) chloride (0.50 g, 1.03 mmol) and sodium diisopropyldithiophosphate (0.24 g, 1.03 mmol) in ~40 ml anhydrous benzene was refluxed for ~6 h. Precipitated sodium chloride was removed by filtration. The solvent was removed under reduced pressure from the filtrate and the yellow solid obtained was crystallized in benzene and dried under reduced pressure (yield = 0.58 g (86%); m.p. = 80 °C).

All other derivatives were prepared by adopting a similar procedure. Pertinent analytical and physicochemical data for these complexes are listed in Table 1.

RESULTS AND DISCUSSION

Syntheses

Bis(dialkyldithiocarbamato)diorganodithiophosphatobismuth(III) complexes have been synthesized by reacting bis(dialkyldithiocarbamato)bismuth(III) chloride with sodium/ammonium diorganodithiophosphates in equimolar ratio in anhydrous benzene by refluxing for ~6 h (Scheme 1).

All the new complexes are either yellow solids or non-volatile yellow/orange-yellow viscous liquids and are soluble in common organic solvents such as benzene, chloroform, carbon disulfide, acetone, dichloromethane, methanol, ethanol, DMSO and DMF.

UV spectra

The electronic absorption spectral data of the new mixed bismuth(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.[7,29] The electronic spectra of these newly synthesized bismuth complexes exhibit three bands. In all the bismuth complexes, the $\pi-\pi^*$ and $n-\pi^*$ transitions are due to dithiophosphate moieties; the $\pi-\pi^*$ intramolecular charge transfer transitions are due to dithiocarbamate moiety overlap and exhibit the most intense broad band at 225–285 nm. The second band appears as a shoulder (305–308 nm) and is assigned to the $\pi-\pi^*$ transition in the N=C=S (dithiocarbamate) group. The third band of low intensity at 345–363 nm is attributed to $n-\pi^*$ or charge transfer transition due to the dithiocarbamate moiety.

Table 1. Physical and analytical data of bis(dialkyldithiocarbamato)diorganodithiophosphatobismuth(III) complexes

Compound (no.) and yield	Colour and state (m.p., °C)	Molecular formula and weight found (calc.)	% Found (Calculated)				
			Bi	S	N	C	H
$[(CH_3)_2NCS_2]_2BiS_2P(OC_2H_5)_2$ (**1**) 91%	Yellow viscous liquid	$C_{10}H_{22}S_6O_2N_2PBi$–(634.60)	32.79 (32.93)	30.13 (30.31)	4.35 (4.41)	18.73 (18.92)	3.57 (3.49)
$[(CH_3)_2NCS_2]_2BiS_2P(OCH_2CH_2CH_3)_2$ (**2**) 90%	Yellow viscous liquid	$C_{12}H_{26}S_6O_2N_2PBi$–(662.62)	31.37 (31.53)	29.21 (29.03)	4.13 (4.22)	21.63 (21.75)	3.87 (3.95)
$[(CH_3)_2NCS_2]_2BiS_2P[(OCH(CH_3)_2]_2$ (**3**) 86%	Yellow solid (80)	$C_{12}H_{26}S_6O_2N_2PBi$ 659 (662.62)	31.43 (31.53)	29.23 (29.03)	4.17 (4.22)	21.86 (21.75)	3.88 (3.95)
$[(CH_3)_2NCS_2]_2BiS_2P[O(CH_2)_3CH_3]_2$ (**4**) 78%	Orange-yellow viscous liquid	$C_{14}H_{30}S_6O_2N_2PBi$–(690.64)	30.16 (30.25)	27.93 (27.85)	3.89 (4.05)	24.24 (24.34)	4.43 (4.37)
$[(CH_3)_2NCS_2]_2BiS_2P[OCH_2CH(CH_3)_2]_2$ (**5**) 93%	Yellow solid (68–70)	$C_{14}H_{30}S_6O_2N_2PBi$ 687 (690.64)	30.08 (30.25)	27.68 (27.85)	4.23 (4.05)	24.56 (24.34)	4.17 (4.37)
$[(CH_3)_2NCS_2]_2BiS_2P(OC_6H_5)_2$ (**6**) 86%	Yellow solid (95–97)	$C_{18}H_{38}S_6O_2N_2PBi$ 712 (730.68)	28.71 (28.60)	26.55 (26.33)	3.67 (3.83)	29.65 (29.58)	3.13 (3.03)
$[(C_2H_5)_2NCS_2]_2BiS_2P(OC_2H_5)_2$ (**7**) 86%	Orange-yellow viscous liquid	$C_{14}H_{30}S_6O_2N_2PBi$–(690.64)	29.99 (30.26)	27.97 (27.88)	3.85 (4.05)	24.44 (24.34)	4.38 (4.34)
$[(C_2H_5)_2NCS_2]_2BiS_2P(OCH_2CH_2CH_3)_2$ (**8**) 82%	Orange-yellow viscous liquid	$C_{16}H_{34}S_6O_2N_2PBi$–(718.66)	29.24 (29.08)	26.99 (26.79)	3.75 (3.89)	26.68 (26.73)	4.89 (4.73)
$[(C_2H_5)_2NCS_2]_2BiS_2P[(OCH(CH_3)_2]_2$ (**9**) 94%	Yellow solid (75–76)	$C_{16}H_{34}S_6O_2N_2PBi$ 726 (718.66)	29.22 (29.08)	26.68 (26.79)	3.95 (3.89)	26.90 (26.73)	4.58 (4.73)
$[(C_2H_5)_2NCS_2]_2BiS_2P[O(CH_2)_3CH_3]_2$ (**10**) 94%	Orange-yellow viscous liquid	$C_{18}H_{38}S_6O_2N_2PBi$–(746.68)	27.87 (27.99)	25.69 (25.79)	3.76 (3.75)	28.91 (28.95)	5.36 (5.08)
$[(C_2H_5)_2NCS_2]_2BiS_2P[OCH_2CH(CH_3)_2]_2$ (**11**) 90%	Orange-yellow viscous liquid	$C_{18}H_{38}S_6O_2N_2PBi$–(746.68)	27.79 (27.99)	26.03 (25.79)	3.80 (3.75)	28.78 (28.95)	5.22 (5.08)
$[(C_2H_5)_2NCS_2]_2BiS_2P(OC_6H_5)_2$ (**12**) 90%	Yellow solid (102)	$C_{18}H_{38}S_6O_2N_2PBi$ 767 (787.32)	26.52 (26.54)	24.50 (24.43)	3.68 (3.55)	33.65 (33.56)	3.79 (3.84)

$$[R'_2NCS_2]_2BiCl + MS_2P(OR)_2 \xrightarrow{\text{Benzene}} [(R'_2NCS_2)_2BiS_2P(OR)_2] + MCl\downarrow$$

(where, R' = Me and Et; R = Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu and Ph; M = Na and NH_4)

Scheme 1. Reaction of bis(dialkyldithiocarbamato)bismuth(III) chloride with sodium/ammonium diorganodithiophosphates in equimolar ratio.

Table 2. The UV spectral data (λ_{max} in nm) of bis(dialkyldithiocarbamato)diorganodithiophosphatobismuth(III) complexes

Compound	Band I	Band II	Band III
1	225–272	308	347
2	228–280	307	353
3	238–285	306	345
4	230–280	305	363
5	230–275	307	355
6	228–277	308	355
7	225–275	305	345
8	230–278	307	355
9	235–280	306	348
10	230–282	305	360
11	235–280	306	352
12	230–285	308	354

IR spectra

The IR spectra (Table 3) of all these new derivatives have been recorded in the range 4000–200 cm^{-1} and tentative assignments of some important characteristic bands have been made on the basis of earlier reports.[6,7,30–34] These bismuth derivatives show strong to medium absorption bands in the regions 1490–1535 cm^{-1} and 1015–1035 cm^{-1} that may be assigned to νC–N and νC–S stretching vibrations, respectively, thus indicating the bidentate nature of the dialkyldithiocarbamate ligand in these complexes.

In addition, the corresponding diorganodithiophosphate ligands show the bands of medium to weak intensity in the regions 955–975 cm^{-1} and 880–895 cm^{-1}, which are assigned to [(P)–O–C] and [P–O–(C)] stretching modes, respectively. A strong band due to P=S stretching vibrations present in the spectra of sodium/ammonium salts of dithiophosphoric acids in the region 660–690 cm^{-1} is shifted towards lower frequencies in the spectra of bis(dialkyldithiocarbamato)diorganodithiophosphatobismuth(III) derivatives and is present at 630–650 cm^{-1}. This shifting indicates most probably a bidentate chelation of dithiophosphate moieties with bismuth. The bands of medium intensities present in the regions 500–540 and 325–350 cm^{-1} are due to P–S and Bi–S stretching vibrations, respectively.

^{1}H NMR spectra

The ^{1}H NMR spectral data (Table 4) of bis(dialkyldithiocarbamato)diorganodithiophosphatobismuth(III) have been recorded in $CDCl_3$ solution using TMS as an internal standard.

In the corresponding dimethyldithiocarbamate derivatives, the methyl protons appear as a singlet between 3.11 and 3.42 ppm, thus suggesting the magnetic equivalence of these protons, whereas the diethyldithiocarbamate derivatives exhibit a triplet or multiplet (overlap with dithiophosphate protons) in the region 1.20–1.45 ppm and a quartet in the region 3.70–3.75 ppm due to CH_3 and CH_2 proton resonances, respectively.

Table 3. The IR spectral data[a] of bis(dialkyldithiocarbamato)diorganodithiophosphatobismuth(III) complexes

Compound	ν(C–N)	ν(C–S)	ν[(P)–O–C]	ν[P–O–(C)]	ν(P=S)	ν(P–S)	ν(Bi–S)
1	1524 s	1025 s	965 m	885 m	635 m	534 m	345 m
2	1505 w	1020 s	957 w	890 w	634 w	528 m	350 w
3	1508 s	1035 s	959 w	886 w	648 w	520 m	335 w
4	1526 w	1023 s	960 w	880 m	645 s	510 w	338 m
5	1516 w	1026 s	970 w	885 w	640 m	505 m	333 w
6	1535 s	1030 s	975 w	895 w	630 s	536 m	347 w
7	1520 s	1022 s	965 m	888 m	630 m	527 m	340 m
8	1513 w	1018 s	958 w	890 w	635 w	523 m	345 w
9	1497 s	1035 s	960 w	882 w	645 w	504 w	325 w
10	1490 w	1015 s	968 w	885 m	640 s	508 w	330 m
11	1510 w	1020 s	970 w	887 w	632 m	540 m	338 w
12	1494 s	1030 s	965 w	885 w	630 s	536 m	327 w

[a] w = weak; m = medium; s = strong.

Table 4. The ^{1}H, ^{13}C and ^{31}P NMR spectral data (δ, ppm)[a] of bis(dialkyldithiocarbamato)diorganodithiophosphatobismuth(III) complexes

Compound	^{1}H NMR chemical shift	^{13}C NMR chemical shift	^{31}P NMR chemical shift
$[(CH_3)_2NCS_2]_2BiS_2P(OC_2H_5)_2$ (**1**)	1.40, t, 6H (CH_3 of dtp) $J = 7.5$ Hz 3.40, s, 12H (NCH_3 of dtc) 4.20, dq, 4H (OCH_2 of dtp) $J(OCH_2CH_2) = 7.5$ Hz $J(POCH_2) = 9.0$ Hz	16.0, d (CH_3 of dtp) J (P, C) = 8.6 Hz 44.0 (NCH_3 of dtc) 63.7, d (OCH_2 of dtp) J (P, C) = 5.6 Hz 200.1 (NCS_2 of dtc)	100.58
$[(CH_3)_2NCS_2]_2BiS_2P(OCH_2CH_2CH_3)_2$ (**2**)	0.93, t, 6H (CH_3 of dtp) $J = 7.5$ Hz 1.53–1.75, m, 4H, (CH_2 of dtp) 3.42, s, 12H, (NCH_3 of dtc) 4.15, dt, 4H (OCH_2 of dtp) $J(OCH_2CH_2) = 7.5$ Hz $J(POCH_2) = 9.0$ Hz	10.5 (CH_3 of dtp) 23.8, d (CH_2 of dtp) J(P, C) = 8.6 Hz 43.5 (NCH_3 of dtc) 68.6, d (OCH_2 of dtp) J (P, C) = 5.6 Hz 200.3 (NCS_2 of dtc)	98.25
$[(CH_3)_2NCS_2]_2BiS_2P[(OCH(CH_3)_2]_2$ (**3**)	1.30, d, 12H[$(CH_3)_2$ of dtp] $J = 7.5$ Hz 3.30, s, 12H (NCH_3 of dtc) 4.75, sep, 2H (OCH of dtp) $J = 7.5$ Hz	23.7, d (CH_3 of dtp) J (P, C) = 4.4 Hz 43.8 (NCH_3 of dtc) 72.8, d (OCH of dtp) J (P, C) = 6.3 Hz 200.6 (NCS_2 of dtc)	96.64
$[(CH_3)_2NCS_2]_2BiS_2P(OCH_2CH_2CH_2CH_3)_2$ (**4**)	0.89, t, 6H (CH_3 of dtp) $J = 7.5$ Hz 1.22–1.37, m, 4H (CH_2CH_3 of dtp) 1.65–1.80, m, 4H (CH_2CH_2O of dtp) 3.30, s, 12H, (NCH_3 of dtc) 4.05, dt, 4H, (OCH_2 of dtp) $J(OCH_2CH_2) = 7.5$ Hz $J(POCH_2) = 9.0$ Hz	13.6 (CH_3 of dtp) 18.8 (CH_2CH_3 of dtp) 32.1, d (α-CH_2 of dtp) J (P, C) = 8.7 Hz 43.8 (NCH_3 of dtc) 67.3, d (OCH_2 of dtp) J (P, C) = 6.6 Hz 200.5 (NCS_2 of dtc)	100.82
$[(CH_3)_2NCS_2]_2BiS_2P[(OCH_2CH(CH_3)_2]_2$ (**5**)	0.86, d, 12H [$(CH_3)_2$ of dtp] $J = 7.5$ Hz 1.88–1.99, m, 2H (CH of dtp) 3.29, s, 12H (NCH_3 of dtc) 3.81, dd, 4H (OCH_2 of dtp) $J(OCH_2CH) = 7.5$ Hz $J(POCH_2) = 9.0$ Hz	18.9 (CH_3 of dtp) 28.8, d (α-CH of dtp) J (P, C) = 8.7 Hz 43.8 (NCH_3 of dtc) 73.6, d (OCH_2 of dtp) J (P, C) = 7.5 Hz 200.1 (NCS_2 of dtc)	101.43
$[(CH_3)_2NCS_2]_2BiS_2P[(OC_6H_5)_2]$ (**6**)	3.11, s, 12H (NCH_3 of dtc) 6.99–7.29, m, 10H (OC_6H_5 of dtp)	43.7 (NCH_3 of dtc) 122–130 (ring carbons of dtp) 200.3 (NCS_2 of dtc)	98.29
$[(C_2H_5)_2NCS_2]_2BiS_2P(OC_2H_5)_2$ (**7**)	1.37, t, 18H (CH_3 of both dtp and dtc) $J = 7.5$ Hz 3.70, q, 8H (NCH_2 of dtc) $J = 7.5$ Hz 4.20, dq, 4H (OCH_2 of dtp) $J(OCH_2CH_3) = 7.5$ Hz $J(POCH_2) = 9.0$ Hz	12.3 (CH_3 of dtc) 16.1, d (CH_3 of dtp) J (P, C) = 8.7 Hz 48.7 (CH_2 of dtc) 63.4, d (OCH_2 of dtp) J(P, C) = 6.2 Hz 198.4 (NCS_2 of dtc)	94.85
$[(C_2H_5)_2NCS_2]_2BiS_2P(OCH_2CH_2CH_3)_2$ (**8**)	0.95, t, 12H (CH_3 of dtp) $J = 7.5$ Hz 1.35, t, 6H (CH_3 of dtc) $J = 7.5$ Hz 1.62–1.75, m, 4H (CH_2 of dtp) 3.75, q, 8H (NCH_2 of dtc) $J = 7.5$ Hz 4.05, dt, 4H (OCH_2 of dtp) $J(OCH_2CH_2) = 7.5$ Hz $J(POCH_2) = 9.0$ Hz	10.2 (CH_3 of dtp) 12.3 (CH_3 of dtc) 23.5, d (α-CH_2 of dtp) J(P, C) = 8.7 Hz 48.6 (CH_2 of dtc) 68.8, d (OCH_2 of dtp) J(P, C) = 6.2 Hz 198.8 (NCS_2 of dtc)	95.97

(*continued overleaf*)

Table 4. (*Continued*)

Compound	^{1}H NMR chemical shift	^{13}C NMR chemical shift	^{31}P NMR chemical shift
$[(C_2H_5)_2NCS_2]_2BiS_2$ $P[(OCH(CH_3)_2]_2$ (**9**)	1.30–1.45, m, 24H (mixing of CH_3 of both dtp and dtc) 3.75, q, 8H (NCH_2 of dtc) $J = 7.5$ Hz 4.87, sep, 2H (OCH of dtp) $J = 7.5$ Hz	12.3 (CH_3 of dtc) 23.8, d (CH_3 of dtp) $J(P, C) = 5.0$ Hz 48.6 (CH_2 of dtc) 72.7, d (OCH of dtp) $J(P, C) = 6.3$ Hz 198.6 (NCS_2 of dtc)	97.21
$[(C_2H_5)_2NCS_2]_2BiS_2$ $P(OCH_2CH_2CH_2CH_3)_2$ (**10**)	0.80, t, 6H (CH_3 of dtp) $J = 7.5$ Hz 1.20–1.45, m, 16H [mixing of CH_3(dtc) and β-CH_2 (dtp)] 1.65–1.75, m, 4H (α-CH_2 of dtp) 3.70, q, 8H (CH_2 of dtc) $J = 7.5$ Hz 4.10, dt, 4H (OCH_2 of dtp) $J(OCH_2CH_2) = 7.5$ Hz $J(POCH_2) = 9.0$ Hz	12.2 (CH_3 of dtc) 13.6 (CH_3 dtp) 18.7 (β-CH_2 of dtp) 32.0, d (α-CH_2 of dtp) $J(P, C) = 8.1$ Hz 48.6 (CH_2 of dtc) 67.0, d (OCH_2 of dtp) $J(P, C) = 14.3$ Hz 198.3 (NCS_2 of dtc)	96.76
$[(C_2H_5)_2NCS_2]_2BiS_2$ $P[(OCH_2CH(CH_3)_2]_2$ (**11**)	0.95, d, 12H (CH_3 of dtp) $J = 7.5$ Hz 1.30, t, 12H (CH_3 of dtc) $J = 7.5$ Hz 1.95–2.05, m, 2H (CH of dtp) 3.75, q, 8H (CH_2 dtc) $J = 7.5$ Hz 3.90, dd, 4H (OCH_2 dtp) $J(OCH_2CH) = 7.5$ Hz $J(POCH_2) = 9.0$ Hz	12.3 (CH_3 of dtc) 19.0 (CH_3 of dtp) 28.9, d (α-CH of dtp) $J(P, C) = 8.6$ Hz 48.7 (CH_2 of dtc) 73.4, d (OCH_2 of dtp) $J(P, C) = 6.8$ Hz 198.5 (NCS_2 of dtc)	98.97

[a] s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; sep = septet; dd = doublet of doublets; dt = doublet of triplets; dtp = diorganodithiophosphate; dtc = dimethyldithiocarbamate.

In addition, these derivatives also exhibit the expected signals due to resonances of the corresponding ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl and phenyl protons of diorganodithiophosphate moieties and are comparable with the earlier reported data.[30–34] The coupling of OCH_2 protons (attached to the carbon atom nearest to the phosphorus atom) with ^{31}P nuclei is also observed in compound numbers 1,2,4,5,7,8,10 and 11 (Table 4).

$\{^1H\}^{13}C$ NMR spectra

The proton-decoupled ^{13}C NMR spectra (Table 4) of these compounds have been recorded in $CDCl_3$ solution using TMS as an internal standard.

The ^{13}C NMR spectra of the dimethyldithiocarbamate complexes show a signal in the region 43.5–44.0 ppm due to NCH_3 carbons. The diethyldithiocarbamate complexes exhibit two signals, one in the region 12.2–12.3 ppm and the other in the region 48.6–48.7 ppm due to CH_3 and CH_2 carbons, respectively. All these compounds show a weak signal between 198.3 and 200.6 ppm due to NCS_2 carbon resonances.

In addition, these derivatives also exhibit the expected signals due to ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl and phenyl carbons of diorganodithiophosphate moieties (Table 4) and are fairly comparable with the data reported earlier.[30–33] The ^{13}C NMR peaks observed for the $S_2P(OR)_2$ moiety, and O- and α-carbons were found as doublets due to coupling with the ^{31}P nucleus.[33,34]

^{31}P NMR spectra

On the basis of the ^{31}P NMR chemical shift values of a number of metal diorganodithiophosphates, Glidewell[35] concluded that complexes showing their NMR signal in the range 82–101 ppm exhibit a bidentate mode of attachment of the dialkyldithiophosphate ligands towards metals. The ^{31}P NMR spectral data for these compounds (Table 4) exhibit only one ^{31}P chemical shift for each compound in the range 94.85–101.43 ppm, indicating the bidentate behaviour of dithiophosphate ligands towards bismuth. The ^{31}P NMR spectral data are comparable with data reported earlier for diorganodithiophosphate complexes.[31–34]

ANTIMICROBIAL ACTIVITY

The free ligands and their bismuth(III) complexes were screened to evaluate their antimicrobial activity against *Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa, Salmonella typhi, Aspergillus niger* and *Penicillium chrysogenum* at three different concentrations; the results are listed in Tables 5 and 6 respectively. The antibacterial activities of some earlier reported antibiotics[36] were compared with our free ligands and their mixed bismuth(III) complexes.

The results showed that the bismuth(III) complexes have lower activity towards all tested bacteria than the free dialkyldithiocarbamate ligand (dtc) and higher activity than the free diorganodithiophosphate ligands (dtp). All the newly synthesized bismuth complexes showed lower activity towards *E. coli* but a considerable effect with other organisms. It may be concluded that the free ligands and bismuth complexes inhibit the growth of bacteria to a greater extent as the concentration is increased.

The antifungal studies showed that the mixed-sulfur ligand bismuth(III) complexes have more or less equal activity towards all tested fungi with the free dialkyldithiocarbamate and higher activity than the free diorganodithiophosphate ligands. It may be concluded that the free ligands and bismuth complexes inhibit the growth of fungi to a greater extent as the concentration is increased.

Nevertheless, it is difficult to make out an exact structure–activity relationship between microbial activity and the structure of these complexes. It can be concluded that the chelation decreases the activity of these complexes.

Comparison of the antimicrobial activities of the free ligands and synthesized complexes with some previously investigated antibiotics[36] shows the following results:

(i) The free ligands (dtc and dtp) and their bismuth(III) compounds show a greater effect towards *S. aureus* compared with amikacin, septrin, cefobid, ampicillin and

Table 5. Antimicrobial activity[a] of free salts of dialkyldithiocarbamate (dtc) and diorganodithiophosphate (dtp) ligands

	Fungi						Gram positive bacteria						Gram negative bacteria								
	A. niger conc. (ppm)			*P. chrysogenum* conc. (ppm)			*S. aureus* conc. (ppm)			*B. subtilis* conc. (ppm)			*E. coli* conc. (ppm)			*P. aeruginosa* conc. (ppm)			*S. typhi* conc. (ppm)		
Ligand	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200
Medtc	++	+++	+++	++	++	+++	++	+++	+++	++	++	+++	+	++	++	+	++	++	++	++	+++
Etdtc	++	+++	+++	++	++	+++	++	+++	+++	++	++	+++	+	++	++	+	++	++	++	+++	+++
Etdtp	+	+	++	+	+	++	+	+	+	+	+	++	0	0	0	0	0	0	0	+	+
^{n}Prdtp	+	+	++	+	+	++	+	+	+	+	+	+	0	0	0	0	0	0	0	+	+
^{i}Prdtp	+	+	+	+	+	+	+	+	+	+	+	+	0	0	0	0	0	0	0	+	+
^{n}Budtp	+	+	++	+	+	++	+	+	+	+	+	+	0	0	0	0	0	0	0	+	+
^{i}Budtp	+	+	++	+	+	+	+	+	+	+	+	++	0	0	0	0	0	0	0	+	+
Phdtp	+	+	++	+	+	++	+	+	+	+	+	++	0	0	0	0	0	0	0	+	+

[a] The test was done using the diffusion agar technique; well diameter = 6 mm; inhibition values beyond control are: +, 1–5 mm; ++ = 6–10 mm; +++, 11–15 mm; 0, not active.

Table 6. Antimicrobial activity[a] of the bis(dialkyldithiocarbamato)diorganodithiophosphatobismuth(III) complexes

	Fungi						Gram positive bacteria						Gram negative bacteria								
	A. niger conc. (ppm)			*P. chrysogenum* conc. (ppm)			*S. aureus* conc. (ppm)			*B. subtilis* conc. (ppm)			*E. coli* conc. (ppm)			*P. aeruginosa* conc. (ppm)			*S. typhi* conc. (ppm)		
Compound	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200
1	++	++	+++	+	++	++	++	++	+++	+	++	++	+	+	++	+	++	++	+	++	++
2	++	++	+++	+	++	++	+	++	++	++	++	+++	+	+	++	++	++	+++	+	++	++
3	+	++	++	++	++	+++	+	++	++	+	++	++	+	+	+	+	+	++	++	++	+++
4	+	++	++	+	++	++	+	++	++	+	++	++	+	+	+	+	++	++	++	++	+++
5	+	++	++	+	++	++	+	++	++	++	++	+++	+	+	+	+	+	++	++	++	+++
6	++	++	+++	++	++	+++	++	++	+++	++	++	+++	+	+	+	+	++	++	++	++	+++
7	++	++	++	++	++	+++	++	++	++	++	++	+++	+	+	+	++	++	+++	++	++	++
8	+	++	++	+	++	++	++	++	+++	++	++	++	+	+	+	++	++	+++	++	++	++
9	+	++	+++	+	++	++	+	++	++	+	++	+++	+	+	+	+	++	++	+	++	++
10	+	++	++	+	++	++	++	++	+++	++	++	+++	+	+	+	++	++	+++	+	++	++
11	++	++	+++	+	++	++	++	++	+++	+	++	++	+	+	+	+	++	++	+	++	++
12	+	++	++	++	++	+++	++	++	+++	++	++	+++	+	+	+	+	++	++	+	++	++
R	+	++	++	+	++	++	+	+	++	+	+	++	+	++	+++	+	++	+++	+	++	+++

[a] The test done was using the diffusion agar technique; well diameter = 6 mm; inhibition values beyond control are: +, 1–5 mm; ++, 6–10 mm; +++, 11–15 mm; 0, not active; R = terbinafin (standard antifungal agent) and chloroamphenicol (standard antibacterial agent).

traivid. However, the free ligands (dtp) and bismuth(III) compounds show a lesser effect towards *S. aureus* compared with doxycillin, augmantin, sulperazon, unasyn, nitrofurantion and erythromycin.

(ii) The *P. aerugunosa* resist the free dtp ligands in three concentrations. The free dtc ligands and bismuth(III) compounds show a greater antibacterial effect towards *P. aerugunosa* than doxycillin, augmantin, unasyn, septrin, cefobid, nitrofurantion, traivid and erythromycin. However, the free dtc ligand and bismuth(III) compounds show a lesser effect towards *P. aerugunosa* compared with amikacin, sulperazon and chloroamphenicol.

(iii) The free dtc ligand and their bismuth(III) complexes show a greater effect towards *E. coli* compared with unasyn, cefobid, ampicillin, erythromycin and dtp ligands (resistance to *E. coli*). However, the free dtc ligand and their bismuth(III) compounds show a lesser effect towards *E. coli* compared with amikacin, doxycillin, augmantin, sulperazon, nitrofurantion, traivid and chloroamphenicol.

(iv) Some bismuth(III) compounds and free ligands (dtc and dtp) show an equal antimicrobial effect to that of some antibiotics.

From all of these results we can conclude that the free ligands and its bismuth complexes show greater antibacterial effects towards some of the investigated antibiotics.

CONCLUSIONS

The preparation, spectroscopic characterization and antimicrobial activity of new mixed sulfur ligand bismuth(III) complexes are presented. The experimental results (IR and NMR) suggest that coordination of the 1,1-dithiolate ligands takes place to make a distorted octahedral geometry of the bismuth with a stereochemically active lone pair of electrons occupying one of the triangular faces of the octahedra.

The biological activity of the free ligands and their bismuth(III) derivatives has been studied by agar diffusion on various microorganisms. All bismuth(III) complexes exhibit an antimicrobial activity comparable with that of the free ligands. The free 1,1-dithiolate ligands (dialkyldithiocarbamate and diorganodithiophosphate) and their mixed bismuth compounds exhibited a higher antibacterial effect than some of the previously investigated antibiotics.

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