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Synthesis, spectroscopic characterization and *in vitro* studies of antimicrobial activity of *bis*(diorganodithiocarbamato)organodithiocarbonatobismuth (III) complexes

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A brief account of the synthesis, spectroscopic characterization and the antimicrobial (bacterial and fungal) behaviour of *bis*(diorganodithiocarbamato)organodithiocarbonatobismuth(III) complexes is presented. The reaction of *bis*(diorganodithiocarbamato)bismuth(III) chloride with potassium organodithiocarbonate in equimolar ratio yielded the corresponding mixed derivatives of the type $[R'_2NCS_2]_2BiS_2COR$ [where, $R' = CH_3$ and C_2H_5; R = Et, Pr^n, Pr^i, Bu^n and Bu^i]. These have been characterized by molecular weight determinations, melting points (only solid complexes) and elemental (C, H, N, S and Bi) analysis as well as spectral IR and NMR [^1H and ^{13}C] studies. The antibacterial and antifungal activities of the free ligands and their bismuth complexes were found *in vitro* by the disc diffusion method. The complexes showed good antibacterial and antifungal effect on some selected bacterial and fungal strains. The antimicrobial activities of two standard antibiotics (Chloroamphenicol and Terbinafin) were also measured and compared with these complexes.

KEYWORDS: bismuth(III) complexes; antibacterial activity; antifungal activity; inhibition zone; diorganodithiocarbamate; organodithiocarbonate; IR; [^1H, ^{13}C] NMR

INTRODUCTION

Diorganodithiocarbamates,[1–4] diorganodithiophosphates,[4,5] and organodithiocarbonates[4,6,7] ligands are versatile in nature and exhibit remarkable diversities in their bonding/coordination patterns (Fig. 1) with main group metals.

Diorganodithiocarbamates have a wide variety of applications such as pesticides (e.g. propineb, zineb, maneb, mancozeb, ziram and thiram), in analytical methods[8,9] as antiviral agents,[10] antidotes for preventing the effects of phytotoxic agents,[11] antimicrobial agents[12] and antitumour drugs.[13] In addition, these types of compounds have important applications in the production of petroleum derivatives, lubricants and polymers, where they are used as accelerators of vulcanization, antioxidants and antihumidity agents.[14,15]

Most of the publications are restricted only to the syntheses and structural characterization of bismuth(III)[16–19] and organobismuth(III)[20] derivatives with these ligands and some of them are fully characterized by single crystal X-ray structural analyses.[7] The corresponding bismuth(III) derivatives with mixed 1,1-dithiolate ligands[21–23] do not appear to have received comparatively less attention of the chemists. In continuation to our recent interest in synthetic and structural aspects of mixed sulfur ligand complexes of main group metals,[21–28] we report herein the syntheses, spectroscopic characterization and antimicrobial activities of the some new mixed sulfur ligand complexes of bismuth(III) of the type $[(R'_2NCS_2)_2BiS_2COR]$ [where, $R' = CH_3$ and C_2H_5; R = Et, Pr^n, Pr^i, Bu^n and Bu^i].

EXPERIMENTAL

Materials and methods

Sodium diorganodithiocarbamates (E. Merck) were used as received. Bismuth trichloride (Fluka) was purified by

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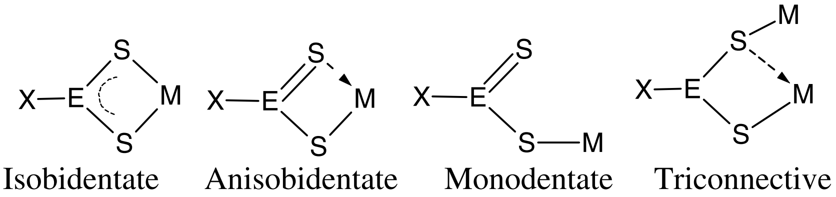

Figure 1. Coordination possibilities of 1,1-dithiolate ligands (where E = C, X = NR_2 and E = C, X = OR).

sublimation before use. The reactants, such as potassium organodithiocarbonate[4] and *bis*(diorganodithiocarbamato) bismuth(III) chloride[29] were prepared by the earlier reported methods. Solvents (benzene, acetone, hexane, diethyl ether, alcohols, etc.) were purified and dried by standard methods[30] before use. Melting points were determined in sealed capillary tubes.

Physical measurements

Bismuth was determined complexometrically by titration against standard EDTA solution using xylenol orange as an indicator, and sulfur was determined gravimetrically as barium sulfate.[31] Molecular weights were determined cryoscopically in benzene. Melting points were determined on B10 Tech India Melting Apparatus and are uncorrected.

The percentages of C, H and N elements were obtained from a Heraeus Carlo Erba 1108 C, H, N analyser. IR spectra were recorded on a Perkin Elmer Model 557 FT-IR spectrophotometer in the range 4000–200 cm^{-1}. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker DRX300 (300 MHz FT-NMR) spectrometer; chemical shift values ^1H and ^{13}C are expressed in δppm relative to TMS.

Synthesis of the bismuth(III) complexes

Bismuth(III) complexes of the general formula $[(R'_2NCS_2)_2 BiS_2COR]$ (where R′ = Me and Et; R = Et, *n*-Pr, *i*-Pr, *n*-Bu and *i*-Bu) were prepared by the reaction of *bis*(diorganodithiocarbamato)bismuth(III) chloride with potassium organodithiocarbonate in molar ratio M:L = 1 : 1. The details of syntheses are as follows.

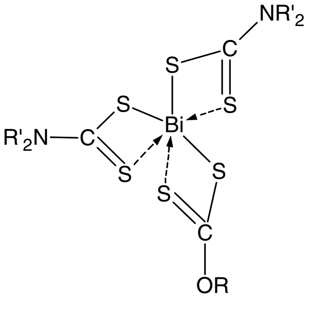

Figure 2. Possible structure of the *bis*(diorganodithiocarbamato)organodithiocarbonatebismuth(III) complexes.

Equimolar amounts of *bis*(diethyldithiocarbamato)bismuth (III) chloride (1.11 g; 2.05 mmol) and potassium isopropyldithiocarbonate (0.35 g; 2.05 mmol) in anhydrous benzene (~20 ml) and carbon disulfide (~20 ml) mixture were stirred for ~4 h at room temperature. Precipitated potassium chloride (0.16 g) was removed by filtration. The solvent was removed under reduced pressure from the filtrate until ~5 ml viscous liquid was left, which was crystallized by adding four to five drops of anhydrous hexane and keeping it overnight in a refrigerator. The yellow crystalline solid was dried under reduced pressure [yield = 0.95 g (71%); m.p. 50 °C]. All the other derivatives were prepared by adopting the similar method. Pertinent analytical and physicochemical data for these complexes are listed in Table 1.

Microbiological studies

Test microorganisms strains

The following strains of two Gram-positive and three Gram-negative bacteria [*Staphylococcus aureus* (ATCC 9144) (G^+), *Bacillus subtilis* (ATCC 6051) (G^+), *Escherichia coli* (ATCC 9637) (G^-), *Pseudomonas aeruginosa* (ATCC 25619) (G^-), *Salmonella typhi* (ATCC 6539) (G^-)] and two fungi [*Aspergillus niger* (ATCC 9029) and *Penicillium chrysogenum* (ATCC 10106)] were screened for their *in vitro* antimicrobial activities.

Method

The compounds were screened for their *in vitro* antimicrobial activities by the well-diffusion method.[27,32] Each compound was dissolved in dimethylformamide (DMF) at a concentration of 50, 100 and 200 ppm. A 0.5 ml spore suspension (10^6–10^7 spore/ml) of each of the investigated organisms was added to a sterile agar 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, then 0.1 ml of tested compounds dissolved in DMF (50, 100 and 200 ppm) were poured into these holes. The incubation time was 24 h at 37 °C for bacteria and 72 h at 30 °C for fungi, after which clear or inhibition zones were detected around each hole. Inhibitory activity was measured (in mm) as the diameter of the inhibition zones.

DMF showed no inhibition zone for all tested microorganisms. For this a quantity of 0.1 ml DMF alone was tested under the same condition for each organism. Terbinafin (standard antifungal agent) and Chloroamphenicol (standard antibacterial agent) were used as references.

Table 1. Physical and analytical data of *bis*(diorganodithiocarbamato)organodithiocarbonatobismuth(III) complexes

Compound no.	Yield (%)	Molecular weight, found (calculated)	m.p., °C	Percentage found (calculated)				
				Bi	S	C	H	N
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH_3$ (**1**)	75	552 (570.64)	72	36.55 (36.62)	33.78 (33.71)	18.79 (18.94)	2.86 (2.97)	4.97 (4.91)
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH_2CH_3$ (**2**)	81	—(584.45)	—	35.88 (35.75)	32.77 (32.91)	20.58 (20.55)	3.18 (3.27)	4.61 (4.79)
$[(CH_3)_2NCS_2]_2BiS_2COCH(CH_3)_2$ (**3**)	79	568 (584.45)	65	35.68 (35.75)	32.97 (32.91)	20.68 (20.55)	3.38 (3.27)	4.68 (4.79)
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH_2CH_2CH_3$ (**4**)	90	583 (598.73)	87	34.83 (34.90)	32.37 (32.16)	22.15 (22.06)	3.41 (3.50)	4.71 (4.67)
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH(CH_3)_2$ (**5**)	86	580 (598.73)	104	35.05 (34.90)	32.02 (32.16)	22.22 (22.06)	3.51 (3.50)	4.61 (4.67)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH_3$ (**6**)	83	607 (626.25)	98	33.46 (33.35)	30.75 (30.69)	24.98 (24.91)	4.14 (4.02)	4.52 (4.47)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH_2CH_3$ (**7**)	84	—(640.56)	—	32.57 (32.62)	29.93 (30.03)	26.35 (26.25)	4.33 (4.24)	4.41 (4.37)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH(CH_3)_2$ (**8**)	71	625 (640.56)	50	32.59 (32.62)	29.98 (30.03)	26.38 (26.25)	4.35 (4.24)	4.46 (4.37)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH_2CH_2CH_3$ (**9**)	96	641 (654.77)	85	31.84 (31.91)	29.22 (29.38)	27.58 (27.51)	4.62 (4.42)	4.30 (4.27)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH(CH_3)_2$ (**10**)	97	639 (654.77)	58	32.05 (31.91)	29.42 (29.38)	27.43 (27.51)	4.33 (4.42)	4.25 (4.27)

RESULTS AND DISCUSSION

Synthesis

Bis(diorganodithiocarbamato)organodithiocarbonatobismuth(III) derivatives were synthesized by reacting *bis* (diorganodithiocarbamato)bismuth(III) chloride with potassium organodithiocarbonate in equimolar ratios in anhydrous benzene and carbon disulfide mixture by stirring at room temperature for ~4 h (Scheme 1).

All these newly synthesized derivatives were yellow solids (except $R = Pr^n$, which were yellow semi-solids) and were soluble in common organic solvents like benzene, chloroform, carbon disulphide, acetone, dichloromethane, DMF and DMSO. The elemental analyses and molecular weights were also in accordance with molecular formulae.

Infrared spectral data

IR spectra (Table 2) of all these newly synthesized compounds were recorded in the range 4000–200 cm^{-1}. Although it was very difficult to differentiate the bands of diorganodithiocarbamate and xanthate, the tentative assignments of the important characteristic bands were made with the help of earlier publications.[18,20–27] The spectra of bismuth(III) derivatives exhibit strong absorption bands in the regions 1200–1225 and 1140–1155 cm^{-1} due to (C–O–C) and (C–O) stretching vibrations, respectively. All these complexes show medium to strong intensity absorption bands in the region 1020–1040 cm^{-1} due to (C–S) stretching vibrations of both diorganodithiocarbamate as well as organodithiocarbonate moieties, indicating the bidentate nature of the both diorganodithiocarbamate and organodithiocarbonate moieties with central bismuth metal (Fig. 2). The complexes also show medium to strong intensity absorption bands in the regions 1490–1515 and 335–350 cm^{-1} due to (C–N) and (Bi–S) stretching vibrations, respectively.

^{1}H NMR spectra

The ^{1}H NMR spectral data of *bis*(diorganodithiocarbamato) organodithiocarbonatobismuth(III) complexes (Table 3) exhibited the expected pattern[18,20–26] without any appreciable shifts. In the corresponding dimethyldithiocarbamate derivatives, the methyl protons appear as a singlet between

$$[R'_2NCS_2]_2BiCl + KS_2COR \xrightarrow{\text{Benzene + CS2}} [R'_2NCS_2]_2BiS_2COR + KCl\downarrow$$

(where, $R' = CH_3$ and C_2H_5; R = Et, Pr^n, Pr^i, Bu^n and Bu^i)

Scheme 1. Reaction of *bis*(diorganodithiocarbamato)bismuth(III) chloride with Potassium organodithiocarbonates in equimolar ratio (1 : 1).

Table 2. IR Spectral data of *bis*(diorganodithiocarbamato)organodithiocarbonatebismuth(III) complexes

Compound	ν(C–N)	ν(C–S)	ν(C–O–C)	ν(C–O)	ν(Bi–S)
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH_3$	1512s	1025s	1205m	1148m	344m
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH_2CH_3$	1505w	1020s	1220w	1153w	350w
$[(CH_3)_2NCS_2]_2BiS_2COCH(CH_3)_2$	1508s	1040s	1209w	1140w	338w
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH_2CH_2CH_3$	1515w	1023s	1210w	1146m	340m
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH(CH_3)_2$	1512w	1026s	1225w	1155w	335w
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH_3$	1505s	1035s	1208w	1148w	349w
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH_2CH_3$	1504s	1022s	1215m	1150m	345m
$[(C_2H_5)_2NCS_2]_2BiS_2COCH(CH_3)_2$	1503w	1028s	1218w	1143w	348w
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH_2CH_2CH_3$	1495s	1035s	1207w	1152w	335w
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH(CH_3)_2$	1490w	1010s	1201w	1146m	342m

w = weak, m = medium, s = strong.

Table 3. ^{1}H and ^{13}C NMR spectral data of *bis*(diorganodithiocarbamato)organodithiocarbonatobismuth(III)

Compound	H^1 NMR chemical shift (δppm)	^{13}C NMR Chemical Shift (δppm)
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH_3$	1.42, t, 3H (CH_3 of xan) $J = 6.6$ Hz 3.35, s, 12H (CH_3 of dtc) 4.64, q, 2H (OCH_2 of xan) $J = 6.6$ Hz	12.4 (CH_3 of xan) 43.3 (CH_3 of dtc) 70.5 (OCH_2 of xan) 195.6 (NCS_2 of dtc) 217.1 (OCS_2 of xan)
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH_2CH_3$	0.98, t, 3H (CH_3 of xan) $J = 6.6$ Hz 1.75-1.85,m,2H (CH_2 of xan) 3.45, s, 12H (CH_3 of dtc) 4.52, t, 2H (OCH_2 of xan) $J = 6.6$ Hz	10.7 (CH_3 of xan) 21.6 (CH_2 of xan) 43.6 (CH_3 of dtc) 79.5 (OCH_2 of xan) 196.9 (NCS_2 of dtc) 217.9 (OCS_2 of xan)
$[(CH_3)_2NCS_2]_2BiS_2COCH(CH_3)_2$	1.05, d, 6H (CH_3 of xan) $J = 6.6$ Hz 3.34, s, 12H (CH_3 of dtc) 5.62, sep, 1H (OCH of xan) $J = 6.6$ Hz	21.6 (CH_3 of xan) 43.8 (CH_3 of dtc) 79.5 (OCH of xan) 198.2 (NCS_2 of dtc) 217.6 (OCS_2 of xan)
$[(CH_3)_2NCS_2]_2BiS_2COCH_2(CH_2)_2CH_3$	0.82, t, 3H (CH_3 of xan) $J = 6.6$ Hz 0.99–1.12, m, 2H (CH_2CH_3 of xan) 1.30–1.42, m, 2H (CH_2CH_2 of xan) 3.42, s, 12H (CH_3 of dtc) 4.35, t, 2H (OCH_2 of xan) $J = 6.6$ Hz	14.3 (CH_3 of xan) 19.1 (CH_2 of xan) 43.5 (CH_3 of dtc) 46.5 (CH_2 of xan) 74.6 (OCH_2 of xan) 197.8 (NCS_2 of dtc) 217.3 (OCS_2 of xan)
$[(CH_3)_2NCS_2]_2BiS_2COCH_2CH(CH_3)_2$	0.82, d, 6H (CH_3 of xan) $J = 6.6$ Hz 1.70–1.83, m, 1H (CH of xan) 3.36, s, 12H (CH_3 of dtc) 4.26, d, 2H (OCH_2 of xan) $J = 6.6$ Hz	14.1 (CH_3 of xan) 32.5 (CH of xan) 43.8 (CH_3 of dtc) 75.6 (OCH_2 of xan) 198.3 (NCS_2 of dtc) 217.2 (OCS_2 of xan)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH_3$	0.65–0.80, m, 15H (CH_3 of dtc and xan) 3.15, q, 8H (CH_2 of dtc) $J = 7.4$ Hz 4.18, q, 2H (OCH_2 of xan) $J = 6.6$ Hz	12.3 (CH_3 of dtc) 14.3 (CH_3 of xan) 48.2 (CH_2 of dtc) 78.7 (OCH_2 of xan) 197.5 (NCS_2 of dtc) 217.8 (OCS_2 of xan)

Table 3. (*Continued*)

Compound	H^1 NMR chemical shift (δppm)	^{13}C NMR Chemical Shift (δppm)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH_2CH_3$	0.68, t, 12H (CH_3 of dtc) $J = 7.4$ Hz	10.6 (CH_3 of xan)
	0.77, t, 3H (CH_3 of xan) $J = 6.6$ Hz	12.2 (CH_3 of dtc)
	1.82-2.05,m, 2H (CH_2 of xan)	20.5 (CH_2 of xan)
	3.25, q, 8H (CH_2 of dtc) $J = 7.4$ Hz	48.6 (CH_2 of dtc)
	4.25, t, 2H (OCH_2 of xan) $J = 6.6$ Hz	76.4 (OCH_2 of xan)
		197.8 (NCS_2 of dtc)
		217.0 (OCS_2 of xan)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH(CH_3)_2$	0.85, t, 12H (CH_3 of dtc) $J = 7.4$ Hz	12.3 (CH_3 of dtc)
	1.06, d, 6H (CH_3 of xan) $J = 6.6$ Hz	21.5 (CH_3 of xan)
	3.25, q, 8H (CH_2 of dtc) $J = 7.4$ Hz	48.7 (CH_2 of dtc)
	5.63, sep, 1H (OCH of xan) $J = 6.6$ Hz	78.3 (OCH of xan)
		198.5 (NCS_2 of dtc)
		217.5 (OCS_2 of xan)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2(CH_2)_2CH_3$	0.70, t, 12H (CH_3 of dtc) $J = 7.4$ Hz	12.4 (CH_3 of dtc)
	0.84, t, 6H (CH_3 of xan) $J = 6.6$ Hz	14.3 (CH_3 of xan)
	1.02–1.13, m, 2H (CH_2CH_3 of xan)	18.9 (CH_2 of xan)
	1.27–1.39, m, 2H (CH_2CH_2 of xan)	48.4 (CH_2 of dtc)
	3.40, q, 8H (CH_2 of dtc) $J = 7.4$ Hz	46.8 (CH_2 of xan)
	4.52, t, 2H (OCH_2 of xan) $J = 6.6$ Hz	74.5 (OCH_2 of xan)
		196.8 (NCS_2 of dtc)
		218.0 (OCS_2 of xan)
$[(C_2H_5)_2NCS_2]_2BiS_2COCH_2CH(CH_3)_2$	0.67–0.82, m, 18H (CH_3 of dtc + xan)	12.3 (CH_3 of dtc)
	1.73–1.85, m, 1H (CH of xan)	14.2 (CH_3 of xan)
	3.38, q, 8H (CH_2 of dtc) $J = 7.4$ Hz	32.7 (CH of xan)
	4.46, d, 2H (OCH_2 of xan) $J = 6.6$ Hz	48.8 (CH_2 of dtc)
		75.7 (OCH_2 of xan)
		197.5 (NCS_2 of dtc)
		217.2 (OCS_2 of xan)

s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sep = septet, dtc = diorganodithiocarbamate, xan = organodithiocarbonate.

3.30–3.45 δppm, thus suggesting the magnetic equivalence of these protons, while the diethyldithiocarbamate derivatives exhibit a triplet at 0.65–0.85 δppm and a quartet at 3.15–3.40 δppm due to CH_3 and CH_2 proton resonances, respectively.

In addition, these derivatives also exhibit the expected signals due to resonances of the corresponding ethyl, *n*-propyl, *i*-propyl, *n*-butyl and *i*-butyl protons of organodithiocarbonate moieties (Table 3) and are comparable with the earlier reported data.[10,17,18]

^{13}C NMR Spectra

The ^{13}C NMR spectra (Table 3) of the dimethyldithiocarbamate complexes show a signal in the region 43.3–43.8 δppm due to NCH_3 carbons. The diethyldithiocarbamate complexes exhibit two signals, one in the region 12.2–12.4 and the other in the region 48.2–48.8 due to CH_3 and CH_2 carbons, respectively. All these compounds show weak signals in the regions 195.6–198.5 and 217.0–218.0 δppm due to NCS_2 and OCS_2 carbon resonances, respectively.

In addition, these derivatives also exhibit the expected signals due to resonances of the corresponding ethyl, *n*-propyl, *i*-propyl, *n*-butyl and *i*-butyl carbons of organodithiocarbonate moieties (Table 3) and are fairly comparable with the data reported earlier.[10,17,18]

ANTIMICROBIAL ACTIVITY

The free ligands (diorganodithiocarbamate and organodithiocarbonate) and their complexes were screened for their antimicrobial activity *in vitro* against five human pathogenic bacterial species and two fungal species at three different concentrations and the results are listed in Table 4 and Table 5, respectively. The antibacterial activities of some earlier reported antibiotics[32] were compared with our free ligands and their mixed bismuth(III) complexes.

The results showed that the bismuth(III) complexes have either less or the same activity towards all tested bacteria and fungi than the free diorganodithiocarbamate ligands but have higher activity than all tested organodithiocarbonates. All the newly synthesized bismuth complexes exhibited lower activity towards *E. coli*, while on other organisms they

Table 4. Antimicrobial activity[a] of the diorganodithiocarbamate and organodithiocarbonate ligands

	Fungi						Gram-positive bacteria						Gram-negative bacteria								
	A. niger Concentration (ppm)			*P. chrysogenum* Concentration (ppm)			*S. aureus* Concentration (ppm)			*B. subtilis* Concentration (ppm)			*E. coli* Concentration (ppm)			*P. aeruginosa* Concentration (ppm)			*S. typhi* Concentration (ppm)		
Compound	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200	50	100	200
Medtc	++	+++	+++	++	++	+++	++	+++	+++	++	++	+++	+	++	++	+	++	++	++	++	+++
Etdtc	++	+++	+++	++	++	+++	++	+++	+++	++	++	+++	+	++	++	+	++	++	++	+++	+++
Etxan	0	+	+	0	+	+	0	+	+	0	+	+	0	0	0	0	0	+	0	+	+
*n*Prxan	0	+	+	0	+	++	0	+	+	0	+	++	0	0	0	0	0	0	0	0	+
*i*Prxan	0	+	+	0	+	+	0	+	+	0	+	+	0	0	0	0	0	+	0	+	+
*n*Buxan	0	+	+	0	+	++	0	+	+	0	+	++	0	0	0	0	0	0	0	0	+
*i*Buxan	0	+	+	0	+	+	0	+	+	0	+	+	0	0	0	0	0	+	0	+	+
R	+	++	++	+	++	++	+	+	++	+	+	++	+	++	+++	+	++	+++	+	++	+++

[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, R = Terbinafin (standard antifungal agent) and chloroamphenicol (standard antibacterial agent).

Table 5. Antimicrobial activity[a] of the *bis*(diorganodithiocarbamato)organodithiocarbonatobismuth(III)

	Fungi						Gram-positive bacteria						Gram-negative bacteria								
	A. niger Concentration (ppm)			*P. chrysogenum* Concentration (ppm)			*S. aureus* Concentration (ppm)			*B. subtilis* Concentration (ppm)			*E. coli* Concentration (ppm)			*P. aeruginosa* Concentration (ppm)			*S. typhi* Concentration (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	+	++	+++	+	++	++	+	++	++	+	++	+++	+	+	+	+	++	++	+	++	++
R	+	++	++	+	++	++	+	+	++	+	+	++	+	++	+++	+	++	+++	+	++	+++

[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, R = Terbinafin (standard antifungal agent) and chloroamphenicol (standard antibacterial agent).

exhibited a considerable effect. It may also be concluded that the free ligands and bismuth complexes inhibit the growth of tested bacterial and fungal species to a greater extent as the concentration is increased.

Comparison of the antimicrobial activities of the free ligands and synthesized mixed sulfur ligand bismuth(III) complexes with some previously investigated antibiotics[30] showed the following results:

(1) The free diorganodithiocarbamate ligands and their bismuth(III) compounds showed a greater activity against Gram-positive bacterial species such as *S. aureus* and *B. subtilis* than chloroamphenicol, while the organodithiocarbonate ligands showed less activity than chloroamphenicol.

(2) For Gram-negative bacterial species, all xanthates were much less active than chloroamphenicol. Diethyldithiocarbamate ligands exhibited greater activity against *S. typhi* while compounds 1, 5 and 7 showed equal activity against *P. aeruginosa* to chloroamphenicol. Compounds 2, 3, 4, 6, 8 and 9 exhibited less activity against *P. aeruginosa* than chloroamphenicol. All complexes showed less activity against *E. coli* and *S. typhi* than chloroamphenicol.

(3) All xanthates were less active against all fungi while diorganodithiocarbamate ligands showed greater activity than Terbinafin. Except for compounds 2, 8 and 10, which were more active against *A. niger* than standard antifungal agent Terbinafin, all complexes showed less activity. Except for compound 2, which was more active against *P. chrysogenum* than standard antifungal agent Terbinafin, all complexes were less active.

From the above results we can conclude that the free dialkyldithiocarbamate ligands showed greater/comparable antibacterial effects to the bismuth complexes. It may possibly be concluded that the chelation decreases the activity of these complexes.

CONCLUSION

The synthesis, spectroscopic characterization and antimicrobial activity of new mixed sulfur ligand bismuth(III) complexes is reported. The absorption bands of medium to strong intensity in the region 1020–1040 $\mathrm{cm^{-1}}$ due to (C–S) stretching vibrations due to both diorganodithiocarbamate as well as organodithiocarbonate moieties indicate the bidentate nature of the both ligands with central bismuth metal and hence a distorted octahedral geometry, with a stereochemically active lone pair of electrons occupying one of the triangular faces of the octahedra, has been tentatively proposed.

Antibacterial and antifungal activities of the free ligands and their bismuth(III) complexes have been studied by agar diffusion method on various microorganisms. All bismuth(III) complexes exhibited antimicrobial activity less than or comparable to that of the free diorganodithiocarbamate ligands and higher than free organodithiocarbonate ligands. Some of the free diorganodithiocarbamates and their mixed bismuth compounds showed higher antimicrobial effect than some of the previously investigated antibiotics.

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REFERENCES

1. Coucouvanis D. *Prog. Inorg. Chem.* 1970; **11**: 233.
2. Manoussakis GE, Kantouri ML, Huff RB. *J. Inorg. Nucl. Chem.* 1975; **37**: 2330.
3. Raston CL, White AH. *J. Chem. Soc. Dalton Trans.* 1976; 791.
4. Garje SS, Jain VK. *Coord. Chem. Rev.* 2003; **236**: 35.
5. Chauhan HPS. *Coord. Chem. Rev.* 1998; **173**: 1.
6. Rao SR. *Xanthates and Related Compounds.* Marcel Dekker: New York, 1971; 7–18.
7. Gupta A, Sharma RK, Bohra R, Jain VK, Drake JE, Hursthouse MB, Light ME. *J. Org. Metal. Chem.* 2003; **678**: 122.
8. Lo CC, Ho MH, Hung MD. *J. Agric. Food Chem.* 1996; **44**: 2227.
9. Verma BC, Sharma DK, Kalia SB, Kumar S. *Pollut. Res.* 1997; **16**: 19.
10. Raston CL, Rowbottom GL, White AH. *J. Chem. Soc. Dalton Trans.* 1981; **6**: 1379.
11. Franekic J, Bratulic N, Pavlica M, Papes D. *Mutat. Res.* 1994; **325**: 65.
12. Safak C, Erdogan H, Ertan M, Yulug N. *J. Chem. Soc. Rak.* 1990; **12**: 296.
13. Aragones J, Lopez-Rodriguez C, Corbi A, Gomez del Arco P, Lopez-Cabrera M, de Landazuri MO, Redondo JM. *J. Biol. Chem.* 1996; **271**: 10 924.
14. Causton BE, Burka FJ, Wilson NH. *Dent. Mater.* 1993; **9**: 209.
15. Johnson DJ, Graham DG, Amarnath V, Amarnath K, Valentine WM. *Chem. Res. Toxicol.* 1996; **9**: 910.
16. Raston CL, Rowbottom GL, White AH. *J. Chem. Soc. Dalton Trans.* 1981; **6**: 1366.
17. Hoskins BF, Tiekink ERT, Winter G. *Inorg. Chim. Acta* 1985; **99**: 177.
18. Snow MR, Tiekink ERT. *Aust. J. Chem.* 1987; **40**: 743.
19. Venkatachalam V, Ramlingam K, Casellato U, Graziani R. *Polyhedron* 1997; **16**: 1211.
20. Wieber M, Rudling HG, Burschka C. *Z. Anorg. Allg. Chem.* 1980; **470**: 171.
21. Chauhan HPS, Singh RK. *Synth. React. Inorg. Met.-Org. Chem.* 2000; **30**: 1211.
22. Chauhan HPS, Singh RK, Kori K. *Main Group Met. Chem.* 2002; **25**: 511.
23. Yin Han-Dong, Wang Chuan-Hua, Wang Y. *Appl. Organometal. Chem.* 2004; **18**: 199.
24. Chauhan HPS, Shaik NM, Kori K. *Main Group Met. Chem.* 2003; **26**: 213.
25. Chauhan HPS, Shaik NM, Kori K. *Synth. React. Inorg. Met.-Org. Chem.* 2004; **34**: 323.
26. Chauhan HPS, Kori K, Shaik NM, Singh UP. *Main Group Met. Chem.* 2004; **27**: 11.
27. Chauhan HPS, Shaik NM. *J. Inorg. Biochem.* 2005; **99**: 538.
28. Chauhan HPS, Kori K, Shaik NM, Mathur S, Huch V. *Polyhedron* 2005; **24**: 89.
29. Preti C, Tosi G, Zannini P. *J. Mol. Struct.* 1979; **53**: 35.
30. Riddick JA, Bunger WB. *Techniques of Chemistry (Organic Solvents)*, Vol. 2. Wiley Inter Science: New York, 1970.
31. Vogel AI. *A Text Book of Quantitative Chemical Analysis*, 5th edn. Bath Press: Bath, 1991; 324 and 490.
32. Mashaly MM, Abd-Elwahab ZH, Faheim AA. *Synth. React. Inorg. Met.-Org. Chem.* 2004; **34**: 233–268.