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Preparation, spectroscopic investigation and antibacterial activity of some organomercury(II) and organotin(IV) dithio complexes

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Phenylmercuric acetate, triphenyltin chloride and dibutyltin chloride react with alkali-metal or ammonium salts of some 1,1- and 1,2-dithio ligands in appropriate molar ratios to yield a series of organometallic dithio complexes of the type [PhHgX] (X = butylxanthate (Buxant$^-$), cyclohexylxanthate (Cyxant$^-$), benzylxanthate (Bzxant$^-$) or pyrrolidin-1-yldithiocarbamate (Pdtc$^-$); [$(PhHg)_2X$] (X = isomaleonitriledithiolate (i-MNT^{2-}) or 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate (ecda^{2-}); Ph_3SnX (X = Buxant$^-$ or Pdtc$^-$); [$(Ph_3Sn)_2$(i-MNT)] and [Bu_2SnMNT] (MNT^{2-} = maleonitriledithiolate). These complexes have been characterized by elemental analysis, molar conductance measurements, IR, FT-Raman, ^1H and ^{13}C NMR and fast atom bombardment (FAB) mass spectra. Cyclic dimeric structures for phenylmercuryxanthates and monomeric structures for the remaining complexes are suggested. Antibacterial activities of the complexes and parent ligands have been screened against some well-known pathogenic bacteria. Organomercury dithiolates have been found to be more potential antibacterial than organotin complexes. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: phenylmercury; organotin; dithio complexes; antibacterial activity

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INTRODUCTION

The importance of organomercury compounds in processes related to global environmental pollution is well known.[1,2] Studies on the abatement of organomercury toxification in naturally occurring biological systems[2,3] have generated much interest in the bio-coordination chemistry of organomercury(II) with sulphur-containing ligands because of the high affinity of mercury for sulphur donor atoms. Therapeutic chelating agents have been used to remove excess metals from the body. In this context dithio ligands as chelating agents could prove potentially useful for removal of organomercurials from the body. Mercury(II)-bound 1,2-dithiolates such as BAL[4] (British anti-Lewisite, 2,3-dimercaptopropanol) and some of its derivatives have been used in the treatment of mercury poisoning. Metal dithiolates and other organometallic chelates have applications in the field of medical science[5–9] as antibacterial, antifungal, antimalarial, antiviral (including anti-HIV) and antitumour agents, and as pesticides, fungicides and bactericides for agricultural purposes.[10] Organotin compounds have also been of interest in environmental[11–14] and biological activities.[15,16]

The interest in such complexes stems not only from their biological and environmental significance but also from their structural characteristics.[17–23]. It was therefore considered useful to synthesize, characterize and assess the antibacterial activity of complexes formed from phenylmercury(II) and organotin(IV) cations with a variety of 1,1- and 1,2-dithio ligands which are not only structurally but also electronically different in spite of having some of their properties in common. A comparison of the antibacterial activity of organomercury and organotin complexes has been carried out. The results of these investigations are reported here.

EXPERIMENTAL

Materials

All experimental manipulations were performed in the open atmosphere. Phenylmercuric acetate, triphenyltin chloride, ethyl cyanoacetate, malononitrile, ammonium pyrrolidinyldithiocarbamate (all from Aldrich), benzyl alcohol, n-butyl alcohol and cyclohexyl alcohol (Fluka) and other analytical reagent grade chemicals were used as received, without further purification. Solvents were purified and distilled adopting standard methods, and where necessary dried before use. The alkali-metal salts of the ligands were prepared by well-established methods. Yellow potassium butylxanthate (KBuxant),[24] sodium cyclohexylxanthate ($NaCyxant{\cdot}2H_2O$) and sodium benzylxanthate (NaBzxant)[25] were prepared by standard methods from the appropriate alcohol, alkali-metal hydroxide/sodium metal and carbon disulphide, and characterized by elemental analysis and IR and NMR spectroscopy. The potassium salts of 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate ($K_2ecda{\cdot}H_2O$)[26] and isomaleonitriledithiolate ($K_2i\text{-}MNT{\cdot}H_2O$)[26] were prepared by literature procedures by the reaction of ethyl cyanoacetate or malononitrile with KOH and CS_2 in dioxane, while disodium maleonitriledithiolate ($Na_2{\cdot}MNT$)[27] was synthesized by the reaction of NaCN, DMF and CS_2 in $CDCl_3$.

Synthesis of organomercury complexes [PhHgX] (X = Buxant$^-$, Cyxant$^-$ or Pdtc$^-$) and [(PhHg)$_2$X] (X = ecda^{2-} or i-MNT^{2-})

Organomercury complexes [PhHgX] and $[(PhHg)_2X]$ were prepared by the reaction of 25 ml of a solution of $PhHg(CH_3COO)$ (0.337 g, 1 mmol) in ethanol–water (80:20, v/v) and 15 ml of a solution of (respectively) KBuxant (0.188 g, 1 mmol), $NaCyxant{\cdot}2H_2O$ (0.234 g, 1 mmol), NaBzxant (0.206 g, 1 mmol) or NH_4Pdtc (0.164 g, 1 mmol) in the same solvent mixture, and by the reaction of 25 ml of (respectively) $PhHg(CH_3COO)$ (0.674 g, 2 mmol) solution with $K_2ecda{\cdot}H_2O$ (0.283 g, 1 mmol) or $K_2i\text{-}MNT{\cdot}H_2O$ (0.236 g, 1 mmol) in the same solvent mixture. In each case, the reaction mixture was stirred for 5 h. The solid products formed were filtered off, washed with ethanol–water, then ethanol, followed by diethyl ether, and recrystallized in an ethanol–acetone mixture and dried over $CaCl_2$ *in vacuo*.

Synthesis of organotin complexes

[Ph_3SnX] (X = Buxant$^-$ or Pdtc$^-$)
To 10 ml of a solution of KBuxant (0.188 g, 1 mmol) or NH_4Pdtc (0.164 g, 1 mmol) in dichloromethane–ethanol (80:20 v/v) was added 10 ml of a saturated solution of Ph_3SnCl (0.385 g, 1 mmol) in the same solvent mixture.

[$(Ph_3Sn)_2$(i-MNT)]
To 20 ml of a solution of $K_2i\text{-}MNT{\cdot}H_2O$ (0.236 g, 1 mmol) was added 10 ml of a saturated solution of Ph_3SnCl (0.77 g, 2 mmol) in the above solvent mixture.

[Bu_2SnMNT]
To 10 ml of a solution of Na_2MNT (0.186 g, 1 mmol) was added slowly 25 ml of a solution of Bu_2SnCl_2 (0.304 g, 1 mmol) in the above solvent mixture.

In each case, the reaction mixture was stirred for 16 h and filtered to remove the KCl/NaCl formed. The filtrate was evaporated to leave a solid residue. The product was washed with ethanol and recrystallized from dichloromethane–ethanol mixture.

Analysis and general methods

Elemental analyses (C, H and N) were performed on a Carlo Erba Analyser MOD 1108. Sulphur was estimated as $BaSO_4$. Conductivity of 10^{-3} M dimethyl sulphoxide (DMSO)/$CHCl_3$ solution of the complexes were measured on a WTW conductivity meter. Melting points were determined in open capillaries using Gallenkamp apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q and Bruker DPX—200 MHz FT-NMR spectrometer using DMSO-d_6 and $CDCl_3$ as solvent. All chemical shifts are reported in parts per million (ppm) downfield from internal reference Me_4Si (TMS). FAB mass spectra were obtained on a JEOL SX 102/DA-6000 mass spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. IR spectra were collected either on a JASCO FT-IR 5300 (4000–400 cm^{-1}) or on a PE 983 (4000–200 cm^{-1}) spectrophotometer, using KBr pellets. The FT-Raman spectra of three samples were collected on a Bruker IFS 66V FT-IR spectrometer FRA 106 Raman module using a YAG laser. The relevant analytical and spectroscopic data are given in Tables 1–4, below.

Table 1 Analytical data and general behaviour of the complexes

Complex (empirical formula)	Colour (% yield)	M.P. (d.p.) (°C)	Found (Calcd) (%)				
			C	H	N	S	Hg/Sn
[PhHgBuxant]	Pale yellow	88–90	30.81	3.25	—	14.82	46.80
($C_{11}H_{14}OS_2Hg$)	(89)		(30.93)	(3.28)		(15.02)	(47.00)
[PhHgCyxant]	Pale yellow	100–102	34.44	3.50	—	13.96	44.15
($C_{13}H_{16}OS_2Hg$)	(94)		(34.45)	(3.53)		(14.16)	(44.31)
[PhHgBzxant]	Pale yellow	137–140	36.35	2.15	—	13.90	43.21
($C_{14}H_{12}OS_2Hg$)	(76)		(36.47)	(2.17)		(13.91)	(43.54)
[PhHgPdtc]	Pale yellow	118–120	31.00	3.00	3.24	15.02	47.00
($C_{11}H_{13}NS_2Hg$)	(85)		(31.15)	(3.07)	(3.30)	(15.13)	(47.34)
[$(PhHg)_2$(i-MNT)]	Yellow	150–151	27.46	1.44	4.00	9.20	57.38
($C_{16}H_{10}N_2S_2Hg_2$]	(96)		(27.61)	(1.44)	(4.03)	(9.22)	(57.70)
[$(PhHg)_2$(ecda)]	Pale yellow	(120–123)	28.99	2.00	1.88	8.65	53.92
($C_{18}H_{15}NO_2S_2Hg_2$)	(82)		(29.10)	(2.02)	(1.89)	(8.64)	(54.05)
[Ph_3SnBuxant]	White	(103–105)	55.24	4.79	—	12.75	23.72
($C_{23}H_{24}OS_2Sn$)	(75)		(55.30)	(4.80)		(12.85)	(23.83)
[Ph_3SnPdtc]	Light yellow	85–90	54.32	4.62	2.80	12.88	23.78
($C_{23}H_{23}NS_2Sn$)	(78)		(54.64)	(4.64)	(2.82)	(12.92)	(23.97)
[$(Ph_3Sn)_2$-(i-MNT)]	Yellow	(218–220)	56.98	3.55	3.35	7.60	27.98
($C_{40}H_{30}N_2S_2Sn$)	(90)		(57.14)	(3.57)	(3.34)	(3.63)	(28.30)
[Bu_2SnMNT]	Brown	(40–45)	38.42	4.81	7.50	17.05	31.74
($C_{12}H_{18}N_2S_2Sn$)	(70)		(38.60)	(4.83)	(7.51)	(17.19)	(31.82)

Antibacterial activity

Evaluation of antibacterial activity of the complexes was divided into two stages:

(1) Screening of the activity by the disc diffusion method;
(2) Quantification of the activity by determining minimum inhibitory concentrations (MICs) by the agar dilution method.

In the first stage, 10 mg ml^{-1} solutions of each of the complexes were prepared in acetone for [PhHgBuxant], [PhHgCyxant], [PhHgBzxant], [PhHgPdtc], [$(PhHg)_2$(i-MNT)] and [Bu_2SnMNT]; in $CHCl_3$ for [Ph_3SnPdtc], Ph_3SnCl, PhHg-(CH_3COO), NH_4Pdtc, KBuxant, NaCyxant and NaBzxant; in DMSO for [$(PhHg)_2$(ecda)], [Ph_3SnBuxant] and [$(Ph_3Sn)_2$(i-MNT)]; and in H_2O for K_2i-MNT, Na_2MNT and K_2ecda. For each of the above compounds, 1 ml of the solution was placed in a vial containing 100 discs of Whatman filter paper No.1 with diameter 6 mm, each absorbing *ca* 0.01 ml of solution. Thus each disc contained *ca* 100 μg of the compound under investigation. Each bacterial strain grown on solid plates was suspended in sterile normal saline with the help of a sterile swab and vortexed to give a homogeneous suspension. The turbidity was matched with McFarland No. 2 system to give 10^6 colony-forming units (CFU) ml^{-1}. The bacteria from this tube were seeded on Muller–Hinton agar with the help of sterile swab to obtain a lawn culture of bacteria by rubbing on the surface of the medium in a criss-cross manner. The prepared impregnated discs were placed on the lawn culture and incubated at 37 °C overnight. Next day the zone of inhibition was observed to determine the antibacterial effect, if any, of a complex.

To determine the MIC of a complex, 20 mg of it was dissolved in 2 ml of the restore respective solvent and then serial double dilution of the compound was carried out 1 ml of each dilution of the individual complex was added to 19 ml of MH agar to obtain the final concentration of 500.00, 250.00, 125.00, 62.50, 31.25, 15.62, 7.81, 3.90, 1.95 and 0.97 μg ml^{-1} on the plate. The bacterial suspensions in saline (described earlier) were seeded with the help of swabs and plates, and incubated for overnight at 37 °C. These plates were examined for the highest dilution which was inhibiting bacterial growth, i.e. the minimum inhibitory concentration (MIC).

$$PhHg(CH_3COO) / Ph_3SnCl + dithiolate^- \rightarrow [PhHgdithiolate] / [Ph_3Sndithiolate] + CH_3COO^- / Cl^- \quad [1]$$

$$2PhHg(CH_3COO) / 2Ph_3SnCl + dithiolate^{2-} \rightarrow [(PhHg)_2(dithiolate)] / [(Ph_3Sn)_2(dithiolate)] + 2CH_3COO^- / 2Cl^- \quad [2]$$

$$Bu_2SnCl_2 + Na_2MNT \rightarrow [Bu_2SnMNT] + 2NaCl \quad [3]$$

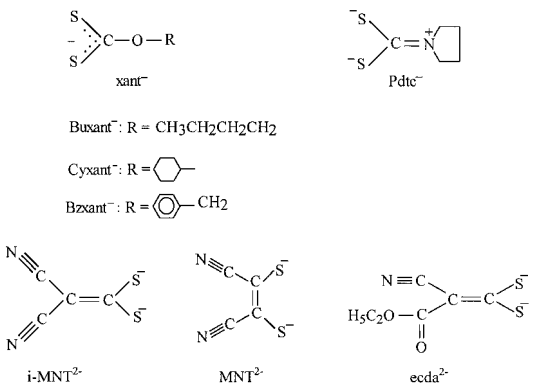

Figure 1 Structure of the ligands: xant = xanthate; Pdtc = pyrrolidin-1-yldithiocarbamate; i-MNT^{2-} = isomaleonitriledithiolate; MNT^{2-} = maleonitriledithiolate; $ecda^{2-}$ = 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate.

RESULTS AND DISCUSSION

Treatment of a solution of $PhHg(CH_3COO)$, Ph_3SnCl of Bu_2SnCl_2 with solutions of ammonium or alkali-metal salts of dithiolates in a 1:1 or 1:2 molar ratio (respectively) resulted in the formation of the organometallic dithio complexes, [PhHgdithiolate] (dithiolate = $Buxant^-$, $Cyxant^-$, $Bzxant^-$ or $Pdtc^-$), [Ph_3Sndithiolate] (dithiolate = $Buxant^-$ or $Pdtc^-$), [$(PhHg)_2$(dithiolate)] (dithiolate = $ecda^{2-}$ or i-MNT^{2-}), [Bu_2SnMNT] and [$(Ph_3Sn)_2$(i-MNT)] according to Equations [1]–[3] (Fig. 1).

The complexes melt or decompose in the temperature range 40–220 °C. Phenylmercury dithiolates are sensitive to light; organotin dithiolates are moisture-sensitive. These complexes are highly soluble in acetone, dichloromethane, chloroform and DMSO but show little solubility in ethanol or methanol. The conductivities (3–15 Ω^{-1} cm^2 mol^{-1}) in 10^{-3} M $CHCl_3$/DMSO indicate their behaviour as nonelectrolytes.

The important IR bands of the complexes along with the Raman bands of [$(PhHg)_2$(i-MNT)], [$(Ph_3Sn)_2$(i-MNT)] and [Ph_3SnBuxant] are presented in Table 2. Dithio ligands coordinate to a metal in a variety of modes such as symmetrical and asymmetrical bidentate, asymmetrical and symmetrical bidentate bridging (and rarely monodentate), yielding complexes of varying nuclearity. A common feature is bidentate coordination. This difference in bonding behaviour can be inferred from the IR spectra. Apart from the bands due to the phenyl and butyl groups, the IR spectra of the

Table 2 Selected infrared [Raman] bands (cm^{-1}) of the complexes[a]

Complex	ν(C≡N) [ν(C=N)]	ν(C=C)	ν(C=O) [ν(C—O)]	ν(C—S)	ν(Hg—C) [ν(Sn—C)]
[PhHgBuxant]	—	—	1235 s	1035 s	670 m, 450 m
[PhHgCyxant]	—	—	1215 s	1020, 1045 m[b]	665 m, 450 w
[PhHgBzxant]	—	—	1190 s	1050 s	690 m, 450 w
[PhHgPdtc]	1440 s	—	—	1000 m, 950 m	690 m, 450 w
[$(PhHg)_2$(i-MNT)]	2205 m (2206 s]	1430 s [1428 s]	—	990 m [996 w] 1020 m [1021 s]	670 m [660 w] 450 m, [455 w]
[$(PhHg)_2$(ecda)]	2195 m	1430 s	1695 s	1140 m	670 m, 455 w
[Ph_3SnBuxant]	—	—	1200 m [1189 w]	1025 w [1023 w] 1000 w [1002 s]	616 w [618 w, 654 m] 460 w [450 w]
[Ph_3SnPdtc]	1420 s	—	—	1035 m 980 m	620 m, 450 m
[$(Ph_3Sn)_2$(i-MNT)]	2200 s [2208 s]	1440 s [1441 s]	—	1050 m [1060 m] 1000 m [999 m]	610 m [614 w] 460 m [450 w]
[Bu_2SnMNT]	2210 s	1440 s	—	1020, 1000 m[b]	595 m, 450 w

[a] Abbreviations: s, strong; m, medium; w, weak.
[b] Split bands.

Table 3 ^{1}H and ^{13}C NMR spectral data of complexes δ (ppm)[a]

Complex	^{1}H NMR	^{13}C NMR
[PhHgBuxant]	0.9 (t, 3H, CH_3), 1.50 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 4.4 (t, 2H, OCH_2), 7.21 (m, 5H, Ar—H)	13.80 (CH_3), 19.10 (CH_2), 30.30 (CH_2), 74.90 (OCH_2), 125.80, 128.30, 128.70, 137.40 (Ar—C), 156.90 (C—O), 222.50 (C—S)
[PhHgCyxant]	1.36 (m, 2H, CH-Cy ring), 1.52 (m, 4H, CH_2-Cy ring), 1.89 (m, 4H, CH_2-Cy ring), 5.26 (m, 1H, CH-Cy ring), 7.45 (m, 5H, Ar—H)	15.70 (CH-Cy ring), 58.72 (CH_2-Cy ring), 90.83 (CH_2-Cy. ring), 122.41 (OCH_2-Cy ring), 125.77, 127.30, 128.00, 137.00 (Ar—C), 166.51 (C—O), 202.00 (C—S)
[PhHgBzxant]	5.6 (s, 2H, OCH_2), 7.4 (m, 10H, Ar—H)	72.38 (OCH_2), 126.61, 126.61, 128.07, 128.40, 138.09 (Ar—C), 142.48 (C—O)
[PhHgPdtc]	2.0 (m, 4H, CH_2-pyrrolidine ring), 3.7 (m, 4H, NCH_2-pyrrolidine ring), 7.5 (m, 5H, Ar—H)	25.95 (CH_2-pyrrolidine ring) 53.04 (NCH_2-pyrrolidine ring) 127.91, 128.00, 128.50, 137.17 (Ar—C)
[$(PhHg)_2$(i-MNT)]	7.3 (m, 10H, Ar—H)	78.00 (C=C), 116.80 (C≡N), 128.38, 128.70, 137.10, 138.00 (Ar—C)
[$(PhHg)_2$(ecda)]	1.4 (t, 3H, CH_3), 4.3 (q, 2H, OCH_2), 7.4 (m, 10H, Ar—H)	13.40 (CH_3), 65.00 (OCH_2), 113.00 (C=C), 127.00 (C≡N), 127.70, 128.00, 137.00, 137.30 (Ar—C)
[Ph_3SnBuxant]	1.2 (t, 3H, CH_3), 2.7 (m, 2H, CH_2), 3.3 (m, 2H, CH_2), 4.4 (t, 2H, OCH_2), 7.2 (m, 15H, Ar—H)	22.92 (CH_3), 24.65 (CH_2), 30.32 (CH_2), 8275 (OCH_2), 127.09, 127.81, 128.29, 136.12 (Ar—C), 156.93 (C—O), 221.4 (C—S)
[Ph_3SnPdtc]	1.9 (m, 4H, CH_2-pyrrolidine ring), 3.5 (m, 4H, NCH_2-pyrrolidine ring), 7.3 (m, 5H, Ar—H)	26.10 (CH_2-pyrrolidine ring), 53.53 (NCH_2-pyrrolidine ring), 128.93, 129.54, 130.87, 131.18 (Ar—C), 193.00 (C—S)
[$(Ph_3Sn)_2$(i-MNT)]	7.4 (m, 30H, Ar—H)	73.00 (C=C), 121.00 (C≡N), 133.70, 133.87, 134.03, 135.11 (Ar—C)
[Bu_2SnMNT]	1.0 (t, 6H, CH_3), 1.6 and 1.8 (m, 12H, (merged peaks of $CH_2.CH_2.CH_2$)	13.91 (CH_3), 25.89 (CH_2), 27.95 (CH_2), 31.19 (CH_2), 117.00 (C=C), 122.00 (C≡N)

[a] Abbreviations: t, triplet; q, quartet; m, multiplet; Ar, aromatic; Cy, cyclohexyl. Solvent: $CDCl_3$ or DMSO-d_6.

complexes show strong bands associated with important functionalities of the dithio ligands, $Buxant^-$, $Cyxant^-$, $Bzxant^-$, $Pdtc^-$, i-MNT^{2-}, $ecda^{2-}$ and MNT^{2-}.

In the case of xanthate complexes the bands observed at 1190–1235 and 1000–1050 cm^{-1} due to ν(C—O) and ν(C—S) modes respectively are consistent with symmetrical bidentate and bidentate-bridging behaviour of the xanthates in the complexes[28] (Fig. 1). On complexation the ν(C—O) band shows a perceptible shift (10–50 cm^{-1}) to high frequency. In the case of pyrrolidinedithiocarbamate complexes, the band at about 1440 cm^{-1} due to ν(C=N) and the presence of distinct bands at around 965 and 1020 cm^{-1} suggest asymmetrical bidentate behaviour of the dithiocarbamate, indicating an increase in the double-bond character of the C–N bond.

IR bands at around 2200, 1430 and 950–1140 cm^{-1} corresponding to ν(C≡N), ν(C=C) and ν(C—S) modes show bidentate/bidentate bridging behaviour of i-MNT^{2-}, $ecda^{2-}$ and MNT^{2-}. Non-involvement of C=O and C≡N groups in bonding is reflected by the almost similar position of these bands in the free ligand as well as in the complexes. It has been observed that the C=C strecthing mode shows a genuine positive shift, while the stretching of the C–S bond in the ligated dinegative dithio ligands is only slightly changed compared with the free ligand, in accordance with the bidentate behaviour of the ligands in these complexes. Invariably, in all of the complexes,

Table 4 FAB mass spectral data in order of decreasing intensity [*m/z*, relative intensity (%), {fragment}$^+$] of the complexes[a]

[PhHgBuxant]	704 (40) [$(PhHg)_2$Buxant]$^+$, 588 (16) [{$(PhHg)_2S$}H]$^+$, 426 (9) [PhHgBuxant]$^+$, 279 (36) [PhHgH]$^+$, 278 (16) [PhHg]$^+$, 79 (100) $[C_6H_7]^+$, 77 (44) [Ph]$^+$, 57 (28) $[C_4H_9]^+$
[PhHgCyxant]	731 (14) [$(M_2$ − Cyxant).H]$^+$, 649 (11) [M_2 − (Cyxant, C_5H_{10} and CH_3)]$^+$, 455 (6) [PhHgCyxant·H_2]$^+$, 453 (6) [PhHgCyxant]$^+$, 232 (27) $[H_2S]^+$, 79 (100) $[C_6H_7]^+$
[PhHgBzxant]	661 (18) [M_2 − (C_6H_5+Bzxant)]$^+$, 461 (2) [PhHgBzxant]$^+$, 232 (37) [HgS]$^+$, 120 (30) [BzCOH]$^+$, 91 (39) [Bz]$^+$, 79 (100) $[C_6H_7]^+$, 31 (25) $[C_2H_7]^+$, 15 (7) $[CH_3]^+$
[PhHgPdtc]	661 (3) [$(PhHg_2CS_2NH{=}CH_2)]^+$, 425 (22) [(PhHgPdtc)H]$^+$, 424 (21) [PhHgPdtc]$^+$, 391 (20) [PhHgPdtc-SH]$^+$, 232 (5) [HgS]$^+$, 77 (22) $[C_6H_5]^+$, 43 (6) $[CH_2NH{=}CH_2]^+$
[$(PhHg)_2$(i-MNT)]	973 (3) [M_2 − (Ph, i-MNT)]$^+$, 696 (13) [M]H$^+$, 391 (42) [PhHg(C_2S_2CN)]$^+$, 270 (19) [Hg(CS)CN]$^+$, 258 (4) [HgCNS]$^+$, 232 (32) [HgS]$^+$, 65 (8) $[CH(CN)_2]^+$
[Ph_3SnPdtc]	496 (4) [Ph_3SnPdtc]$^+$, 422 (94) [(Ph_3SnPdtc) − C_6H_5]$^+$, 351 (76) [Ph_3Sn]$^+$, 266 (8) $[C_4H_8NCS_2SnH]^+$, 114 (84) $[C_4H_8NCS]^+$, 77 (20) [Ph]$^+$, 72 (75) $[C_4H_8NH_2]^+$

[a] Matrix peaks due to *m*-nitrobenzyl alcohol (NBA) were observed at *m/z* 136, 137, 154, 287 and 307. M, monomer; M_2, dimer

bands at around 450 and 660–690 cm^{-1} have been assigned to *v*(Hg—C), while the bands at around 450 and 595–620 cm^{-1} are assigned to *v*(Sn—C) stretching.

A comparison of infrared and Raman bands obtained for [$(PhHg)_2$(i-MNT)], [$(Ph_3Sn)_2$(i-MNT)] and [Ph_3SnBuxant] confirms the assignment of *v*(C≡N), *v*(C═C), *v*(C—S) and *v*(Hg—C)/*v*(Sn—C) bands in the former complexes and *v*(C—O), *v*(C—S) and *v*(Sn—C) modes in the later.

The ^{1}H and ^{13}C NMR spectral data of the complexes are shown in Table 3. All the complexes display resonance signals in aliphatic and aromatic regions characteristic of dithio ligands and phenyl or butyl groups attached to the metal atom, and integrate well for their respective protons.

The positive-ion FAB mass spectral data of the complexes are listed in Table 4. The fragmentation patterns show clear similarity because of the presence of some common fragments in these complexes. In general the fragments containing the metal atom are easily accessible because of their characteristic isotopic patterns. In the case of [PhHgBuxant] a weak peak (*m/z* 426, intensity = 9%) corresponds to the monomeric form while an intense peak (*m/z* 704, 40%) occurs due to loss of one Buxant from the dimeric form of this complex. Similarly, in addition to monomeric molecular ion peaks, [PhHgCyxant] and [PhHgBzxant] generate relatively weak peaks (*m/z* 731, 14%; *m/z* 661, 18%) due to loss of Cyxant and [C_6H_5 + Bzxant] groups from the respective dimeric forms of the complexes. In contrast to organomercury xanthates, PhHgPdtc shows a moderately intense signal (*m/z* 425, *m/z* 22) corresponding to the molecular ion peak reasonable for its monomeric formulation.[29] Similarly, [Ph_3SnPdtc] shows a weak signal (*m/z* 496, 4%) corresponding to the molecular ion peak while an intense signal (*m/z* 422, 94%) shows loss of one phenyl group from the monomer. Another sharp peak (*m/z* 351, 76%) corresponds to the Ph_3Sn^+ moiety in this complex. [$(PhHg)_2$(i-MNT)].H$^+$ gives a signal (*m/z* 696, 13%) due to the molecular ion peak. In addition to the above peaks, several others are also seen in the spectra of the complexes

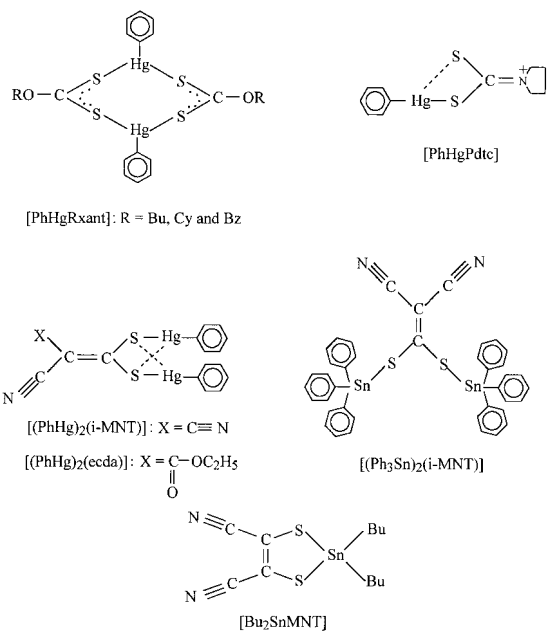

Figure 2 Proposed structures of the complexes.

Table 5 Minimum inhibitory concentration (MIC) of starting compounds by serial dilution method[a]

Bacterial strain	MIC of compounds (μg ml^{-1})			
	NaCyxant[b]	NH_4Pdtc[b]	K_2ecda[c]	Ph_3SnCl[b]
Bacillus subtilis	—	31.25	7.81	500.00
Staphylococcus aureus	—	62.50	7.81	250.00
E. coli	—	62.50	—	0.97
Vibrio cholerae 01 Classical	500.00	31.25	—	—
Shigella boydii	500.00	—	—	—
Klebsiella pneumoniae	500.00	7.81	—	—
Enterobacter species	62.50	15.62	—	—
Proteus vulgaris	62.50	62.50	—	—
Pseudomonas aeruginosa	500.00	125.00	—	—
Salmonella paratyphi B	—	31.25	—	—
Shigella dysenteriae	—	62.50	—	—
Vibrio para haemolyticus	—	31.25	—	—
Salmonella enteritidis	—	62.50	—	—
Aeromonas hydrophila	—	3.91	—	—
Vibrio cholerae non 01	—	62.50	—	—
Shigella flexinerrii	—	62.50	—	—
Shigella sonneii	—	31.25	—	—
Salmonella typhimurium	—	62.50	—	—
Morganella morganii	500.00	62.50	—	—
Serretia narcescens	500.00	62.50	—	—
Citro bacter freundii	62.50	31.25	—	—

[a] Samples were not screened below 0.97 μg ml^{-1}. —, $\geq$500 μg ml^{-1}.
[b] Solvent, $CHCl_3$
[c] Solvent, water.

due to the moieties produced in ionization processes, and several possible reactions with these species. A characteristic fragment for all of the compounds is the base peak (*m/z* 77 or 79) assigned to $C_6H_5^+$ or $C_6H_7^+$. In the case of organomercury complexes, a common peak (*m/z* 232) corresponds to the HgS^+ fragment.

We did not succeed in growing single crystals of the complexes suitable for X-ray analysis. Based on elemental analysis, IR, NMR and FAB mass spectral studies, cyclic dimeric structures[18] for organomerecury xanthates and monomeric structures (Fig. 2) for the remaining complexes[18,21,23] have been suggested.

Antibacterial activity

PhHg(CH_3COO), itself is very toxic against all of the bacteria under study. In general, organometallic dithio complexes show higher activity compared with the starting compounds, Ph_3SnCl and free dithio ligands. Among of the organomercurial complexes, [$(PhHg)_2$(i-MNT)] has the highest potential for bactericidal effects. [PhHgBuxant] also has potential to kill all the bacteria under study, while the starting compounds K_2i-MNT and KBuxant are not effective. Similarly, the starting compound NaCyxant is a less effective bactericide than its organomercurial complex [PhHgCyhxant]. Interestingly, NH_4Pdtc is more effective as such, but on complexation its bactericidal effect diminishes, i.e. there is more bactericidal activity in the ionic from. [PhHgBzxant] also has bactericidal potential against some pathogenic bacteria. Among organotin complexes, [$(Ph_3Sn)_2$(i-MNT)] and [Bu_2SnMNT] show a somewhat broader range of antibacterial activity than [Ph_3SnPdtc] and [Ph_3SnBuxant]. In general organomercury dithio complexes have been found to be more potential antibacterials than organotin dithio complexes. Results are presented in Table 5 and 6.

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Table 6 Minimum inhibitory concentration (MIC) of complexes by serial dilution method[a]

Bacterial strain	MIC of complexes (μg ml^{-1})								
	[PhHg-Buxant][b]	[PhHg-Cyxant][b]	[PhHg-Bzxant][b]	[PhHgPdtc][b]	[$(PhHg)_2$-(i-MNT)][b]	[Ph_3Sn-Pdtc][c]	[$(Ph_3Sn)_2$-(i-MNT)][d]	[PhSn-Buxant][d]	[Bu_2SnMNT][b]
Bacillus subtilis	0.97	31.25	500.00	500.00	0.97	125.00	250.00	62.50	250.00
Staphylococcus aureus	250.00	1.95	500.00	500.00	0.97	125.00	250.00	62.50	0.97
E. coli	500.00	—	500.00	—	3.90	500.00	500.00	250.00	125.00
Vibrio cholerae 01 Classical	0.97	125.00	—	—	1.95	—	—	—	250.00
Shigella boydii	500.00	500.00	—	—	62.50	—	—	—	500.00
Klebsiella pneumoniae	0.97	500.00	500.00	500.00	1.95	—	—	250.00	—
Enterobacter species	0.97	500.00	500.00	500.00	1.95	500.00	250.00	500.00	—
Proteus vulgaris	0.97	—	—	—	3.90	—	—	—	—
Pseudomonas aeruginosa	500.00	—	—	—	250.00	—	—	—	—
Salmonella paratyphi B	500.00	500.00	500.00	500.00	15.62	—	—	—	125.00
Shigella dysenteriae	125.00	—	500.00	—	15.62	500.00	—	—	—
Vibrio parahaemolyticus	500.00	500.00	—	500.00	15.62	500.00	—	—	—
Salmonella enteritidis	500.00	500.00	—	500.00	15.62	—	—	—	250.00
Aeromonas hydrophila	500.00	500.00	500.00	500.00	62.50	500.00	500.00	—	—
Vibrio cholerae non 01	500.00	—	—	—	15.62	500.00	500.00	—	500.00
Shigella flexinerrii	500.00	500.00	0.97	0.97	0.97	—	250.00	—	0.195
Shigella sonneii	500.00	—	—	500.00	3.90	—	—	62.50	—
Salmonella typhimurium	500.00	500.00	—	500.00	3.90	—	500.00	—	—
Morganella morganii	500.00	500.00	—	500.00	15.62	—	250.00	—	—
Serretia marcescens	—	500.00	500.00	500.00	62.50	—	—	250.00	—
Citrobacter freundii	500.00	500.00	500.00	500.00	15.62	—	—	—	—

[a] Samples were not screened below 0.97 μg ml^{-1}. —, $\geq$500 μg ml^{-1}.
[b] Solvent, acetone.
[c] Solvent, $CHCl_3$.
[d] Solvent, DMSO.

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