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Synthesis and Biological Activity of 2-Methylpiperazine-Dithiocarbamato and Di-(2-Methyl-5-Chlorophenyl) Dithiophosphinato Derivatives of Triorganotin(IV) Chloride

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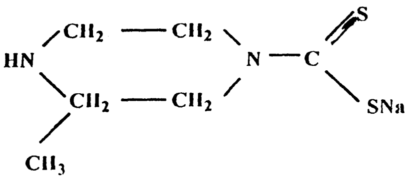
Complexes of triphenyltin(IV) chloride with 2-methylpiperazinedithiocarbamate (Na salt, 2-Mepipzdtc) and di-(2-methyl-5-chlorophenyl) diphosphinate (Na salt; MeCldtpi) have been synthesised and characterised by elemental analysis, IR and ^{1}H-NMR studies. Unlike the symmetrical bidentate nature of the dithiocarbamato group an unsymmetrical bidentate ligation is suggested for the dithiophosphinato group towards organotin(IV) moiety. The thermal stability of the compounds, biological activity against *E. coli* and potential antifungal role of the compounds in wood preservation have been evaluated.

INTRODUCTION

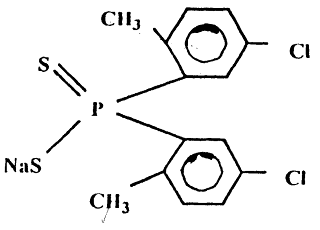
The organotin(IV) derivatives with dithio ligands have been a subject of interest because of their varied structures[1,2] and biocidal activities[3,4]. Unlike other metal dithio derivatives, where the dithio groups are mostly bidentate, in presence of organotin(IV) moiety, the dithio groups behave either as a monodentate or as a bidentate uninegative chelating ligand[5]. Combination of two biocidal groups, the organotin(IV) moiety and organophosphorus or carbamate in the same molecule is likely to produce more potent and lasting biocidal effect. Very few reports are available on triorganotin(IV) derivatives with heterocyclic substituted dithiocarbamates as well as halogen substituted diphenyldithiophosphinates.

EXPERIMENTAL

The sodium salts of 2-methylpiperazinedithiocarbamate (2-Mepipzdtc) and di (2-methyl-5-chlorophenyl) diphosphimate (MeCldtpi) were prepared and purified by the procedure reported elsewhere[6,7]



I. 2-MepipzdtcNa



II. MeCldtpiNa

Preparation of the complexes

(i) *Ph_3Sn(2-mepipzdtc)*: Ethanolic solutions of triphenyltin(IV) chloride (0.01 mol, 50 mL) and the sodium salt of the ligand (0.01 mol, 50 mL) were reacted under vigorous strring conditions over a period of 1 h at room temperature. The white precipitated product was filtered, washed with hot ethanol and recrystallised from 1 : 1 chloroform-ethanol mixture. It was dried over fused $CaCl_2$. Yield *ca.* 66%; m.p. 205°C; Calcd. for $C_{24}H_{26}SnN_2S_2$: Sn, 22.61; S, 12.22; N, 5.33; C, 54.87; H, 4.95%; found: Sn, 22.87; S, 12.63; N, 5.07; C, 54.30; H, 4.67%.

(ii) *Ph_3Sn(MeCldtpi)*: It was prepared by reacting a methanolic solution of triphenyltin(IV) chloride (0.01 mol, 50 mL) with sodium salt of the ligand (0.01 mol, 50 mL) in the same solvent. The reaction mixture was warmed gently up to 45°C on a water bath and stirred vigorously over a period of 1 h. The resulting light yellow compound was filtered, washed with methanol and recrystallised from 1 : 1 methanol-chloroform solution. Like (I) it was dried over fused $CaCl_2$. Yield *ca.* 60%; m.p. 67°C; Calcd. for $C_{33}H_{27}SnCl_2PS_2$: Sn, 17.06; S, 9.21; C, 55.19; H, 3.88%; found: Sn, 16.88; C, 54.82; H, 3.57%.

The elemental analyses for C, H and N were carried out at RSIC, Punjab University, Chandigarh. Metal and sulphur were determined by the reported standard methods[8]. IR spectra were recorded as KBr discs on a Perkin-Elmer 983 spectrophotometer; ^{1}H-NMR spectra in $CDCl_3$ were recorded on a Varian R 3005 spectrometer at RSIC, IIT, Bombay. Thermal analyses (in air) were carried out on a Shimadzu DT-30 thermal analyser.

The antibacterial screening tests of the complexes against *E. coli* were carried out by plate dilution method[9] in agar-agar nutrient broth at pH 7.6. Different concentrations of the complexes were supplemented to the nutrient broth inoculated with 5 × 105 colony forming units of *E. coli* followed by incubation for 24 h at 37°C. The minimum inhibitory concentration (MIC) was found by noting the lowest concentration of the complexes that inhibited the growth (visual turbidity method).

The antifungal screening test of the complexes in B-class wood was carried out by inhibition zone technique[10]. The wood was initially dried in sun and then immersed in a 5% ethanolic solution of the complexes for 48 h, dried and microbial assay was carried out. For antitermite screening test the wood was treated with 5% ethanolic solution of the compound as described above and dried in sun. It was followed by immersing it in a mixture of (1 : 1) kerosene and burnt lube oil for 1 h and dried. The wood pieces were then buried in termite infested moist soil for about six months together with another untreated wood of the same category and exhumed to see how these are eaten by the termites.

RESULTS AND DISCUSSION

The synthesis of the complexes can be represented by the following reactions:

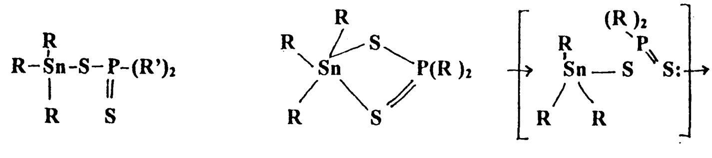
$$\mathrm{Ph_3SnCl + 2\text{-}MepipzdtcNa \longrightarrow Ph_3Sn(2\text{-}Mepipzdtc) + NaCl}$$

$$\mathrm{Ph_3SnCl + MeCldtpiNa \longrightarrow Ph_3Sn(MeCldtpi) + NaCl}$$

The complexes were soluble in common organic solvents and stable at ambient temperature. However, the dithiocarbamato derivative was found to be slightly hygroscopic when exposed to air.

In the IR spectrum of the dithiocarbamato derivative a strong band observed at 1448 cm^{-1} was assigned to $\nu(\mathrm{C{\overset{\cdots}{-}}N})$ which lies intermediate between a $\nu(\mathrm{C{-}N})$ and $\nu(\mathrm{C{=}N})$ suggesting a partial double bond character. Since the saturated heterocyclic ring system has less tendency to release electrons, the $\nu(\mathrm{C{\overset{\cdots}{-}}N})$ band is observed at lower frequency compared to alkyl dithiocarbamate. In the dithiocarbamates the $\nu(\mathrm{C{\overset{\cdots}{-}}N})$ band observed in the 1550–1430 cm^{-1} and $\nu(\mathrm{C{-}S})$ in the 1050–850 cm^{-1} region are known to depend on the nature of coordination with the metal. Splitting of $\nu(\mathrm{C{-}N})$ and $\nu(\mathrm{C{-}S})$ bands are characteristic of a monodentate coordination whereas the appearance of a single band in each region is characteristic of symmetrical bidentate or anisobidentate chelation of the ligand[11]. The appearance of a single band at 1448 cm^{-1} for Ph_3Sn(2-Mepipzdtc) is suggestive of bidentate chelation of the ligand with triorganotin(IV) moiety. Another strong band at 1030 cm^{-1} assigned to $\nu(\mathrm{C{-}S})$ was also indicative of the symmetrical bidentate behaviour of the ligand[1, 12]. The single weak band at 390 cm^{-1} was due to $\nu(\mathrm{Sn{-}S})$ which further corroborates this, as appearance of two $\nu(\mathrm{Sn{-}S})$ indicates unsymmetrical denticity of the sulphur atoms, *i.e.*, two different (M—S) bonds of unequal strength.

In the dithiophosphinato analogue, the bands observed at 645 and 550 cm^{-1} were assigned to $\nu_{asym}(\mathrm{P{-}S})$ and $\nu_{sym}(\mathrm{P{-}S})$ respectively[13]. However, on the basis of the IR data alone, it was difficult to distinguish between the different bonding modes of the MeCldtpi as $\nu(\mathrm{P{-}S})$ and $\nu(\mathrm{P{=}S})$ could not be assigned unequivocally. Further, $\nu(PS_2)$ obscures the $\nu(SnC_3)$ modes. Three different structural possibilities (I–III) can be considered for the complex.



I II III

(R= phenyl, R' = p-chlorotoluene)

The good solubility of the compound in nonpolar organic solvents excluded the possibility of being polymeric (form III). Many dithiophosphato and dithiophosphinato groups are known to behave as bidentate chelate with transition metals[14], but with organotin(IV) moiety the coordination behaviour of the ligand is found to be anisobidentate resulting in different (P—S) and (Sn—S) bond distances due to unequal denticity of the sulphur atoms[14]. On the other hand, the monodentate behaviour (form I) is almost rare[5]. The weak bands observed at 375 and 355 cm^{-1} were attributed to $\nu(\mathrm{Sn{-}S})$ modes which might be indicative of unequal denticity.

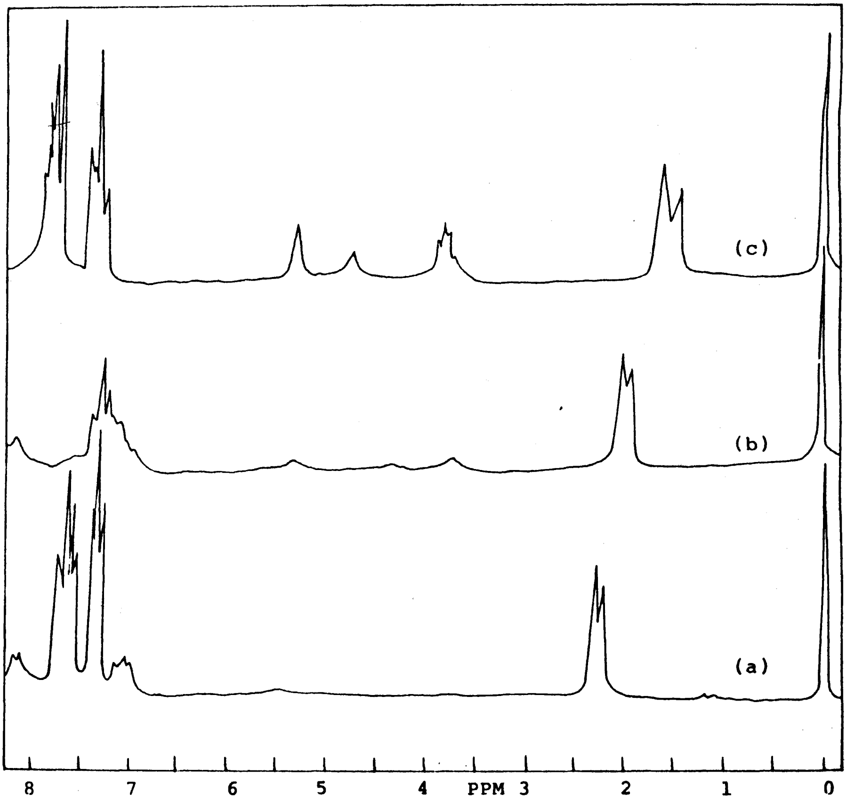


Fig. 1. ^{1}H-NMR spectra of (a) $Ph_3Sn(MeCldtpi)$ (b) MeCldtpiNa and (c) $Ph_3Sn(2\text{-}Mepipzdtc)$

In ^{1}H-NMR spectrum of $R_3Sn(2\text{-}Mepipzdtc)$, the signal for —$CH_2$ protons bonded to distal N-atom was observed at 4.8 ppm while the —CH_2 protons bonded to nitrogen atom of dithiocarbamato group absorbed at 5.4 ppm indicating electron drift towards C—N bond. The phenyl proton signal observed at 7.74 and 7.44 ppm as two sets of multiplets due to *ortho-* and *meta-* protons respectively were in agreement with the penta-coordinated tin(IV) compound with bidentate behaviour of the ligand[15] (Fig. 1).

In $R_3Sn(MeCldtpi)$ the —CH_3 proton signal appeared at 2.3 ppm, intermediate between the pure bidentate (as in diamagnetic $Ni(MeCldtpi)_2$, 2.5 ppm)[16], and monodentate (as in NaMeCldtpi, 2.0 ppm) coordination of the ligand, which was indicative of the anisobidentate nature of the MeCldtpi, the electron flow from sulphur atom being lowered due to unsymmetrical bidentate coordination compared to bidentate one. In the aromatic region the signal at 7.5 ppm was due to ligand protons adjacent to the —CH_3 group while the signal at 8.1 ppm was due to the protons adjacent to the electron withdrawing chlorine atom. However, to confirm the anisobidentate nature of MeCldtpi ligand the ^{119}Sn, ^{31}P-NMR and ^{119}Sn Mossbauer spectral studies will be very useful.

The thermal degradation pattern (TGA) of the compounds (in air medium) indicated that the dithiophosphinato derivative decomposed at a lower temperature (105°C) compared to the dithiocarbamate analogue which decomposed at 210°C. The higher stability of the dithiocarbamato complex is due to its stronger donor capacity compared to dithiophosphinate[17], as in the former there is better metal-ligand $d\pi$-$p\pi$ electron delocalisation. At 270°C an intermediate $(Ph_3Sn)_2S$ was formed which gradually decomposed to SnS at 450°C. In R_3Sn(2-Mepipzdtc) derivative was formed at 307°C and then degraded sharply with evolution of organic matter followed by formation of SnS at 400°C in agreement with earlier investigation on analogous triorganotin(IV) derivative[12].

Both the compounds were found to be bacteriostatic against *E. coli,* the MIC values being 28 μg/mL and 40 μg/mL for R_3Sn(MeCldtpi) and R_3Sn(2-Mepipzdtc) respectively. In the antifungal screening test against wood degrading fungi *Clostridium cumeni* and in antitermitic activity test both compounds inhibit fungal growth and termite attack. The effectiveness of these compounds could be due to the interaction of the nucleic acid component of these organisms with the sulphur ligand (which contains lone pairs) or triorganotin(IV) moiety which is a good acceptor.

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