Snr₂(O₂phph)₂ (R=Me, Bu), Snbu₃o₂phph, Me₄NO₂PHPh.2snph₃cl And Cy₂NH₂SnPh₂(O₂phph)₃: Synthesis and Spectroscopic Studies

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ABSTRACT

Five phenylhydrophosphinato organotin(IV) derivatives and adducts have been synthesized and studied by infrared and Mössbauer techniques. The structures suggested on the basis of spectroscopic data are of discrete, infinite or oligomeric types, the phenylhydrophosphinate anion behaving as a bridging bidentate or a monodentate ligand, the environment around the tin centre being trigonal bipyramidal or octahedral.

Keywords: phenylhydrophosphinato derivatives, ir, Mössbauer, discrete, infinite chains, oligomeric structures

INTRODUCTION

The focus of many research groups in organotin (IV) chemistry is mainly due to the various applications of some molecules of this family including agriculture and industry /1-3/. Shihada and Weller have reported X Ray structures of $SnR_2(Ph_2PO_2)_2$ (R=Ph, Bu) which consist of infinite chains, the environment around the tin centre being octahedral /4/. Several papers dealing with organotin chemistry and the coordinating ability of oxyanions have been reported from our group /5/. In the framework of our search for new organotin compounds, we have initiated here the study of the interactions between $Me_4NO_2PHPh.3H_2O$ or $Cy_2NH_2O_2PHPh$ and SnR_2Cl_2 or SnR_3Cl (R=Bu, Ph), which have yielded five new compounds, infrared and Mössbauer studies of which have been carried out and structures suggested on the basis of spectroscopic data.

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EXPERIMENTAL

 $Me_4NO_2PHPh.3H_2O(L_1)$ and $Cy_2NH_2O_2PHPh(L_2)$ have been obtained on neutralizing PhHPO_2H with a 20% aqueous solution of Me_4NOH or Cy_2NH . Analytical data -% calculated (%found)-($Me_4NO_2PHPh.3H_2O(L_1)$ - C=44.62(44.80); H=8.55(8.60); N=5.21(5.25) $Cy_2NH_2O_2PHPh(L_2)$ -C=66.79(66.69); H=9.20(9.25); N=4.32(4.20).

When $Me_4NO_2PHPh.3H_2O(L_1)$ or $Cy_2NH_2O_2PHPh(L_2)$ in ethanol is mixed with SnR_2Cl_2 (R=Me, Bu) or SnR_3Cl (R=Ph, Bu) in ethanol, white precipitates are obtained and stirred no less than two hours, filtered and washed with hot ethanol.

The analytical data reported below, allow to suggest the following formulae (the ratios L/organotin (IV) are given between brackets):

 $SnMe_{2}(PhHPO_{2})_{2} [1L_{2}/1] (A): C=39.34 (40.24), H=4.31 (4.55)$ $SnBu_{2}(PhHPO_{2})_{2} [1L_{1}/2] (B): C=46.62 (47.03), H=6.10 (6.40)$ $SnBu_{3}PhHPO_{2} [1L_{2}/1] (C): C=50.12(50.39), H=4.30(4.59)$ $Me_{4}NPhHPO_{2}.2SnPh_{3}Cl [1L_{1}/2] (D): C=55.99 (56.15), H=4.87 (4.82), N=1.42 (1.36), Cl=7.20 (7.32)$ $(Cy_{2}NH_{2})SnPh_{2}(O_{2}PHPh)_{3} [2L_{2}/1] (E): C=57.46(57.55); H=5.70(5.83), N=1.59(1.64)$

All the chemicals were purchased from Aldrich Company and used without further purification. The infrared spectra were recorded by means of a PE 580 (4000-200cm⁻¹) or a FTIR-Nicolet (600-50cm⁻¹) spectrometer at the University of Padova (Italy), the sample being as Nujol mulls using CsI or polyethylene windows. Mössbauer spectra were obtained as described previously /6/. Infrared data are given in cm⁻¹ (abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak), (vw) very weak. Mössbauer parameters are given in mms⁻¹ (abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, Γ = full width at half-height).

RESULTS AND DISCUSSION:

Let us consider their ir: (A) vPH 2375s; vPO₂ (1155vs, 1055vs); δ PO₂ 560vs ρ PO₂ 390w; ω PO₂ 330w; v_{as}SnC₂ 585s; vSnO 255w (B): vPH 2350s; vPO₂ (1160vs, 1150vs, 1055vs); δ PO₂ 550vs; ρ PO₂ 385m; ω PO₂ 310w; v_{as}SnC₂ 640m; v_sSnC₂ 617vw; vSnO 205w; (C) vPH 2340m; vPO₂ (1135vs, 1050s); δ PO₂ 550m; ρ PO₂ 385m; ω PO₂ 325w; v_{as}SnC₃ 640s ; v_sSnC₃ 615w; vSnO 210w, (D): vPH 2360m; vPO₂ (1180vs, 1140vs); δ PO₂ 540m ρ PO₂ 370w; ω PO₂ 310w; v_{as}SnC₃ 280m; vSnO 200w; (E) vPH 2380m; vPO₂ (1140vs, 1060s); δ PO₂ 560m ρ PO₂ 370w; ω PO₂ 330w; v_{as}SnC₃ 280m; vSnO 205w and Mössbauer data: (A): δ =1.21mm.s⁻¹ Q.S=4.33 mm.s⁻¹ Γ =0.96 mm.s⁻¹; (B): δ =1.38mm.s⁻¹ Q.S=4.41 mm.s⁻¹ Γ =0.81 mm.s⁻¹; (D): δ =1.29mm.s⁻¹

SnR₂(PhHPO₂)₂ (R=Me, Bu) (A), (B)

The values of the quadrupole splitting of (A) and (B), and the absence of $v_s SnC_2$ in (A) or its appearance (B) as a very weak band at 617 cm⁻¹, are consistent with an almost linear SnR₂ group /7,8/ and allow to suggest for (A) and (B) an infinite chain structure similar to the one reported by Shihada and Weller for SnBu₂(Ph₂PO₂)₂/4/ (Scheme 1).



SnBu₃PhHPO₂ (C)

The presence of $v_s SnC_3$ expected 617 cm⁻¹ on the ir spectrum of $SnBu_3PhHPO_2$ is also an indication of the presence of a trans coordinated $SnBu_3$ group. These features allow to suggest an infinite chain structure, as found for $SnMe_3O_2P(OH)Ph$, or an oligomer (a tetramer) as reported by Newton and al. for $SnMe_3O_2PPh_2$, a pentamer as reported by Ma and al. or an hexamer as reported for $SnMe_3O_2P(OPh)_2$ /9/. We have arbitrarily drawn the infinite chain and the tetramer (Schemes 2a and 2b). Only an X-ray structure determination can precisely give the nucleation- all our attempts to get monocrystals were unsuccessful-.





Me₄NPhHPO₂.2SnPh₃Cl (D)

The value of the quadrupole splitting indicates the coordination of $SnPh_3Cl$ because of its enhancement compared to the value for free $SnPh_3Cl$ (2.55 mm.s⁻¹) /7/ and allows to suggest a discrete structure with a bidentate phenylhydrophosphinate, the environment around the tin (IV) centre being trigonal bipyramidal (Scheme 3).



Scheme 3

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(Cy2NH2)SnPh2(O2PHPh)3 (E)

The value of the quadrupole splitting of (E) indicates the presence of a trans octahedrally coordinated $SnPh_2$ group according to Platt and al. /7/. Let us consider the complex-anion $[SnPh_2(O_2PHPh)_3]^-$ as resulting from an addition of PhHPO₂⁻ on SnPh₂(O₂PHPh)₂. On assuming SnPh₂(O₂PHPh)₂ isostructural to SnPh₂(O₂PPh₂)₂, the suggested structure is an infinite chain obtained on binding PhHPO₂⁻ to the Sn centre;this addition because of steric effects involves a "broadening" of the structure leading to the structure reported in Scheme 4 (the "broadening" has brought the cleavage of one of the bridges of SnPh₂(O₂PHPh)₂ leading to a monocoordinated PhHPO₂⁻).

While considering the interactions between the dicyclohexylammonium ions and the complex-anion $[SnPh_2(O_2PHPh)_3]^-$ through NH-----O hydrogen bonds, responsible of the wide absorption on the ir spectrum of (E) around 2900cm⁻¹, supramolecular architectures are obtained.



Scheme 4

CONCLUSION

In $R_2Sn(O_2HPh)_2$ (R=Me, Bu) the tin centre is in an octahedral environment. $SnBu_3O_2HPh$ contains a bidentate PhHPO₂⁻ anion, the structure being infinite chains or oligomers. The SnPh₃Cl adduct has a discrete structure, while supramolecular architectures are suggested for (Cy₂NH₂)SnPh₂(O₂PHPh)₃

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