2Me₄N₂CO·snPh₂Cl₂: SPECTROSCOPIC STUDIES AN UNEXPECTED IONIC STRUCTURE IN SOLID STATE

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ABSTRACT

A 2:1 tetramethylurea (TMU) diphenyltin dichloride adduct has been synthesized and characterized by elemental analyses, i.r, NMR and Mössbauer spectroscopies. According to the state of the compound (solid or in solution), the structure is ionic or molecular.

INTRODUCTION

In the framework of our search for new organotin compounds¹⁻⁸, we carried out the interactions between tetramethylurea and SnPh₂Cl₂; SnPh₂Cl₂:2TMU has been isolated.

Materials and Methods

Me₄N₂CO (Merck) and diphenyltin dichloride (Aldrich chemicals) are used without further purification. The adduct was obtained after slow solvent evaporation from an ethanolic solution containing Me₄N₂CO and Ph₂SnCl₂ in 2:1 molar ratio. The white powder yielded was recrystallized from methanol. The elemental analyses were performed by the "Service Central d'Analyses" CNRS, Vernaison, France and the Faculty of Chemistry, University of Konstanz, Germany. The i.r and Mössbauer spectra were obtained as described elsewhere⁹. The NMR spectra were recorded in methanol at the "Departamento de Química Física e Química Orgánica", Universidad de Vigo, Spain; and in solid state at the Université Louis Pasteur, Strasbourg, France.

2Me₄N₂CO·Ph₂SnCl₂: Microanalytical data: %calculated (found) C:45.82(45.66); H:05.90(05.98); N:09.72(09.64); Sn:20.60(20.88) Cl:12.32(12.13); m.p: 74°C; yield: 75%. I.r data: 1543(br) νCO 292(s) ν_{as}SnC₂ 220(vs) νSnCl 200(vs) νSnO. Mössbauer data: IS₁ = 1.12 QS₁ = 3.90 IS₂ = 1.58 QS₂ = 3.71 Γ₁ = 1.09 Γ₂ = 1 A₁% = 50 A₂% = 50.

¹H-NMR: δ(phenyl protons)[7.90-7.20(m)(10H)] δ(CH₃) 2.80(s)(24H) ¹³C-NMR: C(CO) 167.4 C(i) 145.3 ¹J=900.6 C(o) 136.2 ²J= 65.0 C(m) 129.8 ³J = 100.2 C(p) 131.1 ⁴J= 35.4 C(CH₃) 38.9. ¹¹⁹Sn-NMR: δ(¹¹⁹Sn) = -228.6; (-375.0 and -330.0 in solid state). The i.r frequencies are in cm⁻¹; ¹H, ¹³C and ¹¹⁹Sn chemical shifts are given in ppm and are referred respectively to TMS (¹H, ¹³C), SnMe₄ (¹¹⁹Sn); the coupling constants ⁿJ(¹¹⁹Sn-¹³C) = ⁿJ are in Hz. Abbreviations: s=strong (i.r) or singlet (NMR), br = broad, vs = very strong, m = complex pattern. Mössbauer parameters are given in mm/s, since the adduct contains two tin centers, QS₁ and QS₂, IS₁ and IS₂, Γ₁ and Γ₂, A₁% and A₂% are respectively the quadrupole splitting, the isomer shift (referred to room temperature SnO₂), the resonance width and the percentage of the first and the second tin site.

RESULTS AND DISCUSSION

On the i.r spectrum (fig.1), the absence of the band due to ν_{as}SnC₂ expected around 230 cm⁻¹⁹ is an indication of the presence of linear (or almost linear) SnC₂ group. The Mössbauer spectrum (fig.2) shows asymmetric and broad peaks which can be better fitted in two doublets in 1:1 area ratio. The linewidth values (higher than 1.08 mm/s) confirm the presence of more than one single tin site. The two doublets can so be ascribed to two different tin centers with similar structural environments. In fact, both QS values (3.90 and 3.71 mm/s) are consistent with a trans hexacoordinated Ph₂Sn residue¹⁰. To explain the presence of two tin sites, we may reasonably consider the presence of an ionic structure resulting from a dimerization of the monomer followed by a resymmetrization leading to [(Me₄N₂CO)₂Ph₂Sn]²⁺[Ph₂SnCl₄]²⁻. The low isomer shift (1.12 mm/s) belonging to the cation while the other one (1.58mm/s) characterizes the anion¹¹. In a previous study¹² related to two complexes containing the diphenyl-tetrachlorostannate dianion, The Mössbauer parameters for each complex were IS = 1.33, QS = 3.55 and IS = 1.30, QS = 3.61 mm/sec, whereas, in the present paper, the corresponding IS and QS values are 1.58 and 3.71 mm/sec. The increase of these values is due to the nature of the cation which contains tin in our case.

Fig.1: Far Infrared spectrum

Fig.2: Mössbauer spectrum

This behaviour in the solid state is confirmed by the solid state ¹¹⁹Sn-RMN (which is a more powerful technique than the Mössbauer) spectrum which exhibits two signals at -375 and -330 ppm. Meanwhile in solution, a single resonance is shown at -228.6 ppm, this value is consistent with a trans hexacoordinated tin environment in solution¹⁰, the ionic structure turns into a molecular one in solution.

All attempts to grow suitable crystals for X-ray diffraction were unsuccessful, but to our best knowledge, it's the first time, a complex of TMU with a tin adduct presents an ionic structure in the solid state on the basis of Mössbauer and solid state Sn NMR, instead of the neutral one generally founded.

The unexpected ionic structure $[(\text{Me}_4\text{N}_2\text{CO})_4\text{Ph}_2\text{Sn}]^{2+}[\text{Ph}_2\text{SnCl}_4]^{2-}$ found in the solid state turns into a molecular structure in solution.

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