Tin(IV) Polymers: Part 2. Synthesis and Structure of Tri(p-substituted Benzyl)tin(IV) Pyridinecarboxylates and Crystal Structure of [(4-FC₆H₄CH₂)₃SnOCO(4-C₅H₄N)₃]∞ and [(4-NCC₆H₄CH₂)₃SnOCO(4-C₅H₄N)·2CH₃CN]∞

Han Dong Yin,¹,² Hao Long Xu,¹ and Qi Bao Wang¹

1. INTRODUCTION

Organotin carboxylates are widely used as biocides, fungicides, and industrial homogeneous catalysts [1–4]. Recently, the pharmaceutical properties of organotin esters of carboxylic acids have been investigated for their anti-tumor activity [5, 6]. Studies of organotin compounds containing carboxylate ligands with additional donor atoms (e.g. N, O or S), which are available for coordinating to tin atom, have revealed that new structural types may lead to different activities [7–10]. As an extension of our studies of organotin carboxylates with additional donor atoms residing on the carboxylate ligand [11], we have synthesized and structurally characterized four triorganotin(IV) pyridinecarboxylates and determined the crystal structures of [(4-FC₆H₄CH₂)₃SnOCO(4-C₅H₄N)₃]∞ and [(4-NCC₆H₄CH₂)₃SnOCO(4-C₅H₄N)·2CH₃CN]∞. The results of the study are reported in this paper.

2. EXPERIMENTAL

2.1. Materials and Measurements

All reactants were reagent grade. The IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs. ¹H- and ¹¹⁹Sn-NMR spectra were obtained with Mercury Plus-400 NMR spectrometer and the chemical shifts are given in ppm relative to Me₄Si and Me₂Sn in CDCl₃. Elemental analyses were performed on a PE-2400-II elemental analyzer. X-ray measurements were made on a Bruker Smart-1000 CCD...
differatometer with a graphite monochromatic MoKα (0.71073 Å) radiation.

2.2. Synthesis of Compounds 1–6

All the compounds were synthesized using similar procedure as shown in Scheme 1. A mixture of bis[tri(p-substituted benzyl)tin] oxide (1.0 mmol) and pyridinecarboxylic acid (2.0 mmol) were refluxed in dry benzene (30 ml) for 6–7 h. The liberated water was removed azeotropically with a Dean-Stark apparatus. The clear solution obtained after filtration was evaporated under vacuum to give a white solid. The products were recrystallized from dichloromethane–hexane mixture to give colorless crystals.

(a) [(4-FC₆H₄CH₂)₃Sn(O₂C(3-C₅H₄N))]ₙ (1): Yield 82%, m.p. 138–139 °C, ¹H-NMR (CDCl₃), δ ppm (integration, multiplicity/coupling constant, assignment): 9.20 (3H, s, 2-Py–H), 8.74 (3H, br, 6-Py–H), 8.34 (3H, br, 5-Py–H), 7.30 (3H, br, 3-Py–H), 6.85–7.42 (4H, m, Ar–H), 2.90 (6H, s, J_Sn-H = 71 Hz, SnCH₂). IR (KBr mull) cm⁻¹ (assignment): ν_as(COO), 1632; ν_s(COO), 1351; ν(Sn–C), 557; ν(Sn–N), 486; ν(Sn–O), 462. Anal. Calcd. for C₇₂H₂₃Cl₇NO₅Sn: C, 52.49; H, 3.56; N, 2.27; Found: C, 52.62; H, 3.60; N, 2.32.

(b) [(4-FC₆H₄CH₂)₂Sn(O₂C(4-C₅H₄N))]ₙ (2): Yield 85%, m.p. 167–169 °C, ¹H-NMR (CDCl₃), δ ppm (integration, multiplicity/coupling constant, assignment): 9.15 (3H, s, 2-Py–H), 8.73 (3H, br, 6-Py–H), 8.32 (3H, br, 5-Py–H), 7.33 (3H, br, 3-Py–H), 6.83–7.42 (4H, m, Ar–H), 2.90 (6H, s, J_Sn-H = 71 Hz, SnCH₂). IR (KBr mull) cm⁻¹ (assignment): ν_as(COO), 1634; ν_s(COO), 1352; ν(Sn–C), 558; ν(Sn–N), 490; ν(Sn–O), 457. Anal. Calcd. for C₇₂H₂₄Cl₇NO₅Sn: C, 57.08; H, 3.90; N, 2.46; Found: C, 57.21; H, 3.83; N, 2.42.

(c) [(4-CIC₆H₄CH₂)₃Sn(O₂C(3-C₅H₄N))]ₙ (3): Yield 76%, m.p. 145–147 °C, ¹H-NMR (CDCl₃), δ ppm (integration, multiplicity/coupling constant, assignment): 9.22 (3H, s, 2-Py–H), 8.71 (3H, br, 6-Py–H), 8.27 (3H, br, 5-Py–H), 7.53 (3H, br, 3-Py–H), 7.53–7.46 (4H, m, Ar–H), 2.94 (6H, s, J_Sn-H = 70 Hz, SnCH₂). IR (KBr mull) cm⁻¹ (assignment): ν_as(COO), 1632; ν_s(COO), 1351; ν(Sn–C), 557; ν(Sn–N), 486; ν(Sn–O), 462. Anal. Calcd. for C₇₂H₂₄Cl₇NO₅Sn: C, 52.49; H, 3.56; N, 2.27; Found: C, 52.62; H, 3.60; N, 2.32.

(d) [(4-ClC₆H₄CH₂)₂Sn(O₂C(4-C₅H₄N))]ₙ (4): Yield 85%, m.p. 180–182 °C, ¹H-NMR (CDCl₃), δ ppm (integration, multiplicity/coupling constant, assignment): 8.73 (2H, d, 2,6-pyridine–H), 7.84 (2H, d, 3,5-Py–H), 7.49–7.47 (4H, m, Ar–H), 2.68 (6H, s, J_Sn-H = 69 Hz, ArCH₂Sn). IR (KBr mull) cm⁻¹ (assignment): ν_as(COO), 1641; ν_s(COO), 1358; ν(Sn–C), 581; ν(Sn–N), 500; ν(Sn–O), 465. Anal. Calcd. for C₇₂H₂₄Cl₇NO₅Sn: C, 52.49; H, 3.56; N, 2.27; Found: C, 52.33; H, 3.70; N, 2.25.

(e) [(4-NCC₆H₄CH₂)₂Sn(O₂C(4-C₅H₄N))]ₙ (5): Yield 78.5%, m.p. 144–146 °C, ¹H-NMR (CDCl₃), δ ppm (integration, multiplicity/coupling constant, assignment): 9.07 (3H, s, 2-Py–H), 8.70 (3H, br, 6-Py–H), 8.18 (3H, br, 5-Py–H), 7.52 (3H, br, 3-Py–H), 7.10–7.38 (4H, m, Ar–H), 2.86 (6H, s, J_Sn-H = 70 Hz, SnCH₂). IR (KBr mull) cm⁻¹ (assignment): ν_as(COO), 1631; ν_s(COO), 1346; ν(Sn–C), 548; ν(Sn–N), 487; ν(Sn–O), 451. Anal. Calcd. for C₇₂H₂₄Cl₃NO₅Sn: C, 61.15; H, 3.77; N, 9.51; Found: C, 61.40; H, 3.67; N, 9.62.

(f) [(4-NCC₆H₄CH₂)₂Sn(O₂C(4-C₅H₄N))₂CH₂CN]ₙ (6): Yield 77%, m.p. 179–181°C, ¹H-NMR (CDCl₃), δ ppm (integration, multiplicity/coupling constant, assignment): 8.67 (2H, d, 2,6-Py–H), 7.69 (2H, d, 3,5-Py–H), 7.04–7.33 (12H, m, Ar–H), 2.87 (6H, s, J_Sn-H = 73 Hz, ArCH₂Sn), 2.00 (6H, s, CH₃CN). IR (KBr mull) cm⁻¹ (assignment): ν_as(COO), 1640; ν_s(COO), 1348; ν(Sn–C), 538; ν(Sn–N), 485; ν(Sn–O), 450. Anal. Calcd. for C₇₄H₂₅Cl₄NO₇Sn: C, 60.83; H, 4.20; N, 12.52. Found: C, 60.95; H, 3.80; N, 12.69.

2.3. Crystallographic Measurements of Compounds 2 and 6

X-ray crystallographic data for the compounds 2 and 6 were collected on a Bruker smart-1000 CCD diffractometer using MoKα radiation (0.71073 Å). The structure was solved by the direct method and difference Fourier map using the SHELX-97 program, and refined by full-matrix least squares on F². All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically. The details are given in Table I.