Synthesis and in vitro Fungicidal Study of Organotin(IV) Complexes of Monomethyl Glutarate

W. Rehman*, M. K. Baloch*, A. Badshah**, and S. Ali**
*Department of Chemistry, Gomal University, Dera Ismail Khan, Pakistan
**Department of Chemistry, Quaid-e-Azam University, Islamabad, Pakistan

e-mail: sono_waj@yahoo.com

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Abstract—The synthesis and study of new coordination compounds of some organotin(IV) chlorides with monomethyl glutarate are reported. The ligand molecule appears to be bound to the tin atom through the carboxylic oxygen. The results obtained from $^1$H, $^{13}$C, and $^{119}$Sn NMR, FT-IR and $^{119}$Sn Mössbauer spectra show that the complexes are pentacoordinated with the trigonal bipyramidal structure. Biological screening of organotin(IV) derivatives shows promising activity, especially for the triphenyltin complex exhibiting higher antifungal activity. In addition, the rest of the compounds also prove to be active against various fungi used.

INTRODUCTION

The chemistry of organotin(IV) complexes has witnessed quantum leap during the past few decades. They have wide applications as catalysts, stabilizers, biocides, antifouling agents, and wood preservers [1–5]. Investigations have also been carried out to find their application as antitumour agents. It has been noted that, indeed, several di- and triorganotin(IV) species, particularly, organotin(IV) carboxylates, are found to be active against various types of cancer [5–7].

In the past few years, a number of biologically important organotin(IV) complexes have been prepared by our research group [8–12]. As a continuation of our interest in organotin(IV) carboxylates we are now reporting the synthesis, spectroscopic characterization, and in vitro fungicidal activity of a series of triorganotin(IV) complexes of monomethyl glutarate.

EXPERIMENTAL

All triorganotin(IV) compounds, except tribenzyltin chloride, were purchased from Fluka and used as received. Tribenzyltin chloride was synthesized by a described method [13]. All the reactions were carried out under anhydrous and oxygen-free nitrogen atmosphere. The solvents were dried before use according to the literature method [14]. The melting points were measured on a Reichert thermometer (F.G. Bode Co. Austria). IR spectra were obtained in KBr using a Perkin-Elmer FT IR-1605 spectrophotometer in a range of 400–4000 cm$^{-1}$. Elemental analyses were carried out on a Yanaco MT-3 high-speed CHN analyzer with an antipyrene as a reference compound. The amount of tin was determined using an inductively coupled plasma atomic emission spectrometry (ICP-AES) method on an ARL 3410 instrument. The $^1$H, $^{13}$C, and $^{119}$Sn NMR spectra were recorded on a multinuclear FT NMR (200 MHz) JEOL instrument using TMS as an internal standard. Some of the $^{13}$C spectra were measured on a Bruker AM 270 instrument at 50 MHz with a $^{13}$C probe. Mössbauer spectra were recorded at 80 K on a Cryophysics instrument equipped with a 15 mCi Ca$^{119}$SnO$_3$ source.

Synthesis of Monomethyl Glutarate (HL)

Glutaric anhydride (50 mmol) was refluxed in excess dry methanol for 10 h under anhydrous conditions; excess solvent was removed under reduced pressure, resulting a yellow oil. The yield was 85%.

For C$_6$H$_{10}$O$_4$Sn ($M = 146$)
al. calcd (%): C 49.27, H 6.80.
Found (%): C 49.29, H 6.82.

$^1$H NMR (CDCl$_3$, δ, ppm): 3.5 (s., H-1), 2.5 (t., H-3), 2.3 (q., H-4) 2.0 (t., H-5), 12.6 (s., H-6).

$^{13}$C NMR (CDCl$_3$, δ, ppm): 52.1 (C-1), 173.8 (C-2), 30.2 (C-3), 29.5 (C-4), 31.5 (C-5), 174.5 (C-6).

IR (KBr, cm$^{-1}$): 1720 – ν(C=O), 2065 – ν(OH).

Synthesis of Trimethyl, Tributyl, Triphenyl, and Tribenzyltin Complexes of Monomethyl Glutarate (I–IV)

The monomethyl glutarate (5 mmol) was dissolved in a minimum amount of methanol (25 ml). To this triethyl amine (5 mmol) was added, and the reaction mix-

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1 The text was submitted by the authors in English.
ture was refluxed for 10–30 min, a hot methanolic solution of trimethyl-, tributyl-, triphenyl-, or tribenzyltin chloride (5 mmol) was added to the above reaction mixture, and this mixture was refluxed for 8–9 h under nitrogen. The reaction mixture was centrifuged and filtered to remove triethylaminechloride; and excess solvent was removed under reduced pressure. Liquid complexes were formed for trimethyl- and tributyltin chloride, while solid complexes were obtained for triphenyl- and tribenzyltin, which were recrystallized from a 1:2 (vol/vol) mixture of methanol and petroleum ether (b.p. 40–60°C).

I: The yield was 75%, colorless liquid; Λ, Ω−1 cm² mol⁻¹ (10⁻³ M methanol): 2.1.

For C₉H₁₈O₄Sn (M = 310)
anal. calcd (%): C 34.82, H 5.80, Sn 38.69.
Found (%): C 34.84 H 5.81, Sn 38.71.

¹H NMR (CDCl₃, δ, ppm): 3.2 (s., H-1), 2.4 (t., H-3), 2.6 (q., H-4) 2.0 (t., H-5), 0.5 (s., H-α).

¹³C NMR (CDCl₃, δ, ppm): 51.9 (C-1), 173.8 (C-2), 30.3 (C-3), 29.6 (C-4), 29.1 (C-5), 176.8 (C-6); –2.5 (C-α), 1J¹¹⁹Sn–¹³C = 555 Hz).

IR (KBr, cm⁻¹): 1630s—νₐr(OOC); 1454br—νₐr(OOC); Δν = 176; 1722s—ν(C=O), 520br—ν(Sn–C), 566sh—ν(Sn–O).

¹¹⁹Sn Mössbauer (CDCl₃, mm/s): quadrupole splitting (QS): 3.78 ± 0.05; isomeric shift (IS): 1.28 ± 0.01; Γ₁: 1.10; Γ₂: 1.12.

II: The yield was 70%, colorless liquid; Λ, Ω−¹ cm² mol⁻¹ (10⁻³ M methanol): 2.3.

For C₂₄H₂₄O₄Sn (M = 436)
anal. calcd (%): C 49.52, H 8.25, Sn 27.50.
Found (%): C 49.54 H 8.26, Sn 27.52.

¹H NMR (CDCl₃, δ, ppm): 3.3 (s., H-1), 2.5 (t., H-3), 2.5 (q., H-4) 1.9 (t., H-5), 0.5 (s., H-α), 1.32 (m., H-β and H-γ).

¹³C NMR (CDCl₃, δ, ppm): 52.1 (C-1), 174.1 (C-2), 30.7 (C-3), 29.8 (C-4), 31.2 (C-5), 177.2 (C-6); 26.7 (C-α), 1J¹¹⁹Sn–¹³C = 560 Hz), 25.3 (C-β), 2J¹¹⁹Sn–¹³C = 18 Hz), 24.9 (C-γ), 3J¹¹⁹Sn–¹³C = 59.5 Hz), 13.3 (C-δ).

IR (KBr, cm⁻¹): 1642s—νₐr(OOC); 1440br—νₐr(OOC); Δν = 194; 1730—ν(C=O), 547w—ν(Sn–C), 572sh—ν(Sn–O).

¹¹⁹Sn NMR (CDCl₃, δ, ppm): –171.

¹¹⁹Sn Mössbauer (CDCl₃, mm/s): QS: 3.90 ± 0.05; IS: 1.43 ± 0.01; Γ₁: 0.96; Γ₂: 0.98.

III. The yield was 78%, solid, m.p. = 107°C; Λ, Ω−¹ cm² mol⁻¹ (10⁻³ M methanol): 2.8.

For C₂₄H₂₄O₄Sn (M = 496)
anal. calcd (%): C 57.90, H 4.82, Sn 24.50.
Found (%): C 58.06, H 4.84, Sn 24.19.

¹H NMR (CDCl₃, δ, ppm): 3.3 (s., H-1), 2.7 (t., H-3), 2.6 (q., H-4) 2.1 (t., H-5), 7.8 (m., H-α), 7.6 (m., H-β), 7.75 (m., H-γ), 7.80 (m., H-δ).

¹³C NMR (CDCl₃, δ, ppm): 52.3 (C-1), 174.5 (C-2), 31.1 (C-3), 30.2 (C-4), 31.6 (C-5), 178.8 (C-6); 126.3 (C-α), 1J¹¹⁹Sn–¹³C = 690 Hz), 130.7 (C-β), 2J¹¹⁹Sn–¹³C = 22 Hz), 129.2 (C-α), 3J¹¹⁹Sn–¹³C = 62 Hz), 128.5 (C-δ).

IR (KBr, cm⁻¹): 1638s—νₐr(OOC), 1454br—νₐr(OOC), Δν = 174, 1720s—ν(C=O), 540w—ν(Sn–C), 563sh—ν(Sn–O).

¹¹⁹Sn NMR (CDCl₃, δ, ppm): –98.5.

¹¹⁹Sn Mössbauer (CDCl₃, mm/s): QS: 3.15 ± 0.05; IS: 1.22 ± 0.01; Γ₁: 1.36; Γ₂: 1.41.

IV. The yield was 80%, solid, m.p. = 121°C; Λ, Ω−¹ cm² mol⁻¹ (10⁻³ M methanol): 2.5.

For C₂₇H₃₆O₄Sn (M = 538)
anal. calcd (%): C 60.20, H 5.55, Sn 22.27.
Found (%): C 60.22, H 5.57, Sn 22.30.

¹H NMR (CDCl₃, δ, ppm): 3.5 (s., H-1), 2.5 (t., H-3), 2.4 (q., H-4) 2.0 (t., H-5), 2.1 (s., H-α), 7.75 (m., H-β), 7.70 (m., H-γ), 7.72 (m., H-δ), 7.80 (H-ω).

¹³C NMR (CDCl₃, δ, ppm): 51.8 (C-1), 174.7 (C-2), 30.9 (C-3), 30.4 (C-4), 32.2 (C-5), 175.8 (C-6); 29.6 (C-α), 1J¹¹⁹Sn–¹³C = 570 Hz), 134.3 (C-β), 2J¹¹⁹Sn–¹³C = 20 Hz), 128.5 (C-γ), 3J¹¹⁹Sn–¹³C = 57 Hz), 125.5 (C-δ), 123.5 (C-ω).

IR (KBr, cm⁻¹): 1632—νₐr(OOC), 1460—νₐr(OOC), Δν = 172, 1722s—ν(C=O), 522br—ν(Sn–C), 566sh—ν(Sn–O).

¹¹⁹Sn NMR (CDCl₃, δ, ppm): –150.

¹¹⁹Sn Mössbauer (CDCl₃, mm/s): QS: 3.89 ± 0.01; IS: 1.41 ± 0.01; Γ₁: 0.88; Γ₂: 0.86.