Inorganica Chimica Acta 423 (2014) 177–182

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, spectral characterization, antibacterial and antitumor studies of some diorganotin(IV) complexes derived from 2-phenylmonomethylglutarate

Wajid Rehman [a,*], Amin Badshah [b], Fazal Rahim [a], Musa Kaleem Baloch [c], Hameed Ullah [a], Obaid-Ur-Rahman Abid [a], Mohsan Nawaz [a], Isfahan Tauseef [d]

[a] Department of Chemistry, Hazara University, Mansehra, Pakistan
[b] Department of Chemistry Quaid-e-Azam University, Islamabad, Pakistan
[c] Department of Chemistry, University of Sargodha, Bhakkar Campus, Bhakkar, Pakistan
[d] Department of Microbiology, Hazara University, Mansehra, Pakistan

ARTICLE INFO

Article history:
Received 1 May 2014
Received in revised form 10 July 2014
Accepted 6 August 2014
Available online 13 August 2014
SI: Antitumor Active Organotin Compounds

Keywords:
2-Phenylmonomethylglutarate
Antitumor
Antibacterial
Organotin(IV)

ABSTRACT

A novel series of diorganotin(IV) complexes of the type R_2SnL_2 (R = Me, Et, Bu, Ph Bz and L = 2-phenylmonomethylglutarate) has been reported herein. The synthesized compounds has been characterized by elemental analysis and their solid state configuration has been determined by various spectroscopic (IR, ^{1}H, ^{13}C, ^{119}Sn NMR, ^{119m}Sn Mössbauer) techniques. The results obtained are in full agreement with the proposed 2:1 stoichiometry. The title complexes have been screened against various Gram positive and Gram negative bacteria and human cell line KB, the results obtained showed that the diphenyltin(IV) complex exhibited excellent activity against all types of bacteria, while diethyltin(IV) complex was found to have promising antitumor activity.

1. Introduction

The chemistry of organotin(IV) complexes has observed a dramatic rise during the last few eras. They have been practiced for their *in vitro* activity against a large variety of tumor lines and found to be as effective as conventional heavy metal antitumor drugs such as Cisplatin [1]. In addition to the aforementioned uses, organotin compounds are also important in prospect of their broad structural diversity. This feature has been attracting the interest of a number of scientists and an enormous amount of structural types have been uncovered [2,3]. There has been considerable interest in the chemistry of penta- and hexacoordinated organotin(IV) complexes derived from various organic ligands due to their structural and stereochemical properties, in obvious contrast to the well documented chemistry of organotin(IV) complexes [4–6]. Organotin(IV) complexes are put to use in various fields and exhibit potential biological applications such as bactericidal, insecticidal, fungicidal and antitumor activities. Organotin compounds are now the active components in a number of biocidal formulations, finding applications in such diverse areas as fungicides, miticides, molluscicides, marine antifouling paints, surface disinfectants and wood preservatives [7–9]. In order to magnify the scope of investigations on the coordination behavior of various donor ligands towards organotins, we carried out the investigations and established their bioactivities [10–15]. As an extension of this research field, we are now interested in the development of the chemistry of some novel organotin compounds obtained by the interaction of a number of diorganotin(IV) halides with the 2-phenylmonomethyl glutarate.

2. Experimental

All the diorganotin(IV) compounds except dibenzyltin dichloride were purchased from Merck and were used as such. Dibenzyltin dichloride was synthesized through a known method [16]. The solvents used were dried before use according to the prescribed method [17]. Melting point was measured on a Reichert thermometer of F.G. Bode Co. Austria. IR spectra were obtained in KBr using Perkin Elmer FT IR –1605 spectrophotometer. An elemental analysis was carried out on a Yanaco MT-3 high-speed CHN analyzer with an antipyrine as a reference compound. The amount of tin

---

* Corresponding author. Tel.: +92 997 414136; fax: +92 997 530046.
E-mail address: sono_waj@yahoo.com (W. Rehman).

http://dx.doi.org/10.1016/j.ica.2014.08.006
0020-1693/

was determined using an inductively coupled plasma atomic emission spectrometry (ICP-AES) on ARL 3410. The ^{1}H ^{13}C and ^{119}Sn NMR spectra were recorded on a multinuclear FT NMR 300 MHz of Bruker Biospin using TMS (^{1}H and ^{13}C) and Me_4Sn (^{119}Sn) as an internal standard. The Mössbauer spectra were recorded at 80 K on a Cryophysics instrument equipped with a 15 mCi $Ca^{119}SnO_3$ source.

2.1. Synthesis of 2-phenylmonomethylglutarate (ligand)

The 2-phenylglutaricanhydride (50 mmol) was refluxed in excess of dry methanol for 10 hours under anhydrous conditions; excess of solvent was removed under reduced pressure. The white solid obtained as *2-phenylmonomethylglutarate.* Quantities of the reactants used were 11.12 g, (50 mmol) 2phenylglutaricanhydride, excess of methanol, physical state: white solid, mp = 83 °C Yield: 75% Recrystallization solvent: chloroform/petroleum ether.

Elemental analysis: calculated/found (%) for Elemental analysis: calculated/found (%) for $C_{12}H_{14}O_4$ (222) C 64.86 (64.84); H 6.30 (6.29).

Molar conductance (Methanol, 10^{-3} M): 0.5 Ω^{-1} cm^2 mol^{-1}.

IR (KBr cm^{-1}): 3010s (νCH aromatic); 1725s (νC=O); 2072m (ν COOH).

^{1}H NMR ($CDCl_3$): H-2: 7.4–7.5m [2H, phenyl protons]; H-3: 7.1–7.2m [2H, phenyl protons]; H-4: 7.2–7.3m [2H, phenyl protons]; H-5: 7.2–7.3m [2H, phenyl protons]; H-6: 7.4–7.5m [2H, phenyl protons]; H-7: 4.3s [1H, CH]; H-8: 2.1t [J = 10.0 and 5.0 Hz, 2H, CH_2]; H-9: 2.5t [10.0 and 5.0 Hz, 2H, CH_2]; H-11: 11.9s [1H, OH]; H-13: 3.1s[3H, OMe].

^{13}C NMR ($CDCl_3$): C-1: 137.5; C-2: 125.9; C-3: 128.4; C-4: 126.1; C-5: 130.2; C-6: 128.9; C-7: 50.22; C-8: 26.35; C-9: 35.15; C-10: 177.7; C-11: 175.5; C-12: 58.4.

2.2. Synthesis of tin (IV) complexes

The ligand (10 mmol) was dissolved in minimum amount of methanol (25 mL) in a three neck round bottom flask equipped with reflux condenser, thermometer and a drying tube. To this triethylamine (10 mmol) was added and stirred, the stoichiometric amount of diorganotin dichloride (5 mmol) in methanol (25 mL), added drop wise with constant stirring for 10–30 min. The reaction mixture was then refluxed for 8 h under nitrogen. After cooling the reaction was centrifuged and filtered to remove the triethylamine chloride. The filtrate was concentrated under vacuum. The solid complexes obtained, were recrystallized from a 1:2(v/v) mixture of methanol and petroleum ether (b.p 40–60 °C). Very fine crystals were obtained as final product. Ours attempts to obtain single crystal suitable for XRD were failed.

2.2.1. Synthesis of dimethyltin bis(2-phenylmonomethylglutarate) ***1***

Quantities of the reactants used were 2.22 g, (10 mmol) 2phenylmonomethylglutarate; 1.1 g; (5 mmol) dimethyltin dichloride and 2 g, (10 mmol) triethylamine. Physical state: amorphous solid; recrystallization solvent: chloroform/petroleum ether; mp = 108 °C; Yield: 68%.

Elemental analysis: calculated/found (%) for Elemental analysis: calculated/found (%) for $C_{26}H_{32}O_8$ (592) C 52.70 (52.68); H 5.40 (5.39); Sn 20.27 (20.25).

Molar conductance (Methanol, 10^{-3} M): 1.2 Ω^{-1} cm^2 mol^{-1}.

IR (KBr cm^{-1}): 3030w (νCH aromatic); 1620sr (νOCO)$_{asym}$; 1388med (νOCO)$_{sym}$; $\Delta\nu$ = 242; 1720sr (νC=O); 535sr (ν Sn–C); 478sh (ν Sn–O).

^{1}H NMR ($CDCl_3$): H-2: 7.4–7.5m [2H, phenyl protons]; H-3: 7.3–7.4m [2H, phenyl protons]; H-4: 7.3–7.4m [2H, phenyl protons]; H-5: 7.2–7.3m [2H, phenyl protons]; H-6: 7.4–7.5m [2H, phenyl protons]; H-7: 4.8s [1H, CH]; H-8: 2.2t [10.0 and 5.0 Hz, 2H, CH_2]; H-9: 2.5t [10.0 and 5.0 Hz, 2H, CH_2]; H-11: A; H-13: 3.3s[3H, OMe]; H-α: 1.4s [6H, 2CH_3] $^{2}J(^{119}Sn–^{1}H)$ = 82 Hz.

^{13}C NMR ($CDCl_3$): C-1: 137.7; C-2: 126.1; C-3: 128.5; C-4: 126.4; C-5: 130.5; C-6: 129.1; C-7: 50.3; C-8: 26.5; C-9: 35.2; C-10: 177.9; C-11: 175.7; C-12: 58.5; C-α: 2.4 ^{1}J ($^{119}Sn–^{13}C$) = 748 Hz.

^{119}Sn NMR ($CDCl_3$): −330 ppm.

^{119}Sn Mössbauer ($CDCl_3$, mm/s): Q.S: 3.75 ± 0.01; I.S: 1.24 ± 0.03; Γ_1: 0.95; Γ_2: 1.01.

2.2.2. Diethyltin bis(2-phenylmonomethylglutarate) ***2***

Quantities of the reactants used were 2.22 g, (10 mmol) 2phenylmonomethylglutarate; 1.53 g, (5 mmol) dimethyltin dichloride and 2 g, (10 mmol) triethylamine. Physical state: amorphous solid; recrystallization solvent: chloroform/petroleum ether; mp = 115 °C; Yield: 73%.

Elemental analysis: calculated/found (%) for Elemental analysis: calculated/found (%) for $C_{28}H_{36}O_8Sn$ (620) C 54.19 (54.18); H 5.80 (5.78); Sn 19.36 (19.35).

Molar conductance (Methanol, 10^{-3} M): 1.5 Ω^{-1} cm^2 mol^{-1}.

IR (KBr cm^{-1}): 3030w (νCH aromatic); 1638sr (νOCO)$_{asym}$; 1390med (νOCO)$_{sym}$; $\Delta\nu$ = 248; 1724sr (νC=O); 538sr (ν Sn–C); 482sh (ν Sn–O).

^{1}H NMR ($CDCl_3$): H-2: 7.5–7.6m [2H, phenyl protons]; H-3: 7.4–7.5m [2H, phenyl protons]; H-4: 7.3–7.4m [2H, phenyl protons]; H-5: 7.4–7.5m [2H, phenyl protons]; H-6: 7.5–7.6m [2H, phenyl protons]; H-7: 4.4s [1H, CH]; H-8: 2.2t [10.0 and 5.0 Hz, 2H, CH_2]; H-9: 2.6t [10.0 and 5.0 Hz, 2H, CH_2]; H-11: A; H-13: 3.4s[3H, OMe]; H-α: 1.3q [4H, 2CH_2] $^{2}J(^{119}Sn–^{1}H)$ = 87 Hz.; H-β: 1.4t [6H, 2CH_3].

^{13}C NMR ($CDCl_3$): C-1: 137.7; C-2: 126.1; C-3: 128.5; C-4: 126.4; C-5: 130.5; C-6: 129.1; C-7: 50.3; C-8: 26.5; C-9: 35.2; C-10: 177.9; C-11: 175.7; C-12: 58.5; C- α: 9.2 ^{1}J ($^{119}Sn–^{13}C$) = 755 Hz. C-β: 15.2 ^{1}J ($^{119}Sn–^{13}C$) = 25 Hz.

^{119}Sn NMR ($CDCl_3$): −315 ppm.

^{119}Sn Mössbauer ($CDCl_3$, mm/s): Q.S: 3.78 ± 0.01; I.S: 1.29 ± 0.03; Γ_1: 0.91; Γ_2: 1.20.

2.2.3. Dibutyltin bis(2-phenylmonomethylglutarate) ***3***

Quantities of the reactants used were 2.22 g, (10 mmol) 2phenylmonomethylglutarate; 1.24 g, (5 mmol) dibutyltin dichloride and 2 g, (10 mmol) triethylamine. Physical state: amorphous solid; recrystallization solvent: chloroform/petroleum ether; mp = 128 °C; Yield: 85%.

Elemental analysis: calculated/found (%) for Elemental analysis: calculated/found (%) for $C_{32}H_{44}O_8Sn$ (676) C 56.80 (56.78); H 6.50 (6.49); Sn 17.75 (17.73).

Molar conductance (Methanol, 10^{-3} M): 1.9 Ω^{-1} cm^2 mol^{-1}.

IR (KBr cm^{-1}): 3030w (νCH aromatic); 1640sr (νOCO)$_{asym}$; 1390med (νOCO)$_{sym}$; $\Delta\nu$ = 250; 1730sr (νC=O); 542sr (ν Sn–C); 485sh (ν Sn–O).

^{1}H NMR ($CDCl_3$): H-2: 7.5–7.6m [2H, phenyl protons]; H-3: 7.4–7.5m [2H, phenyl proton]; H-4: 7.3–7.4m [2H, phenyl protons]; H-5: 7.4–7.5m [1H, phenyl proton]; H-6: 7.5–7.6m [2H, phenyl protons]; H-7: 4.4s [1H, CH]; H-8: 2.2t [10.0 and 5.0 Hz, 2H, CH_2]; H-9: 2.6t [10.0 and 5.0 Hz, 2H, CH_2]; H-11: A; H-13: 3.5s[3H, OMe]; H-α: 1.2m [4H, 2CH_2] $^{2}J(^{119}Sn–^{1}H)$ = 85 Hz; H-β: 1.3m [4H, 2CH_2] $^{3}J(^{119}Sn–^{1}H)$ = 25 Hz ; H-γ: 1.3m [4H, 2CH_2]; H-δ: 1.5t [6H, 2CH_3].

^{13}C NMR ($CDCl_3$): C-1: 137.7; C-2: 126.3; C-3: 128.4; C-4: 126.6; C-5: 130.5; C-6: 129.3; C-7: 50.4; C-8: 26.6; C-9: 35.3; C-10: 178.1; C-11: 176.1; C-12: 58.7; C- α: 23.5 ^{1}J ($^{119}Sn–^{13}C$) = 765 Hz. C-β: 25.2 ^{2}J (^{119}Sn-^{13}C) = 25 Hz; C-γ: 24.5 ^{3}J ($^{119}Sn–^{13}C$) = 55 Hz; C-δ: 12.5 ($^{119}Sn–^{13}C$) = n.o.

^{119}Sn NMR ($CDCl_3$): −305 ppm.

^{119}Sn Mössbauer ($CDCl_3$, mm/s): Q.S: 3.80 ± 0.01; I.S: 1.29 ± 0.03; Γ_1: 0.97; Γ_2: 1.15.