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Synthesis and Characterisation of Diorganotin(IV) Complexes of 3,4-Dihydroxybenzaldehyde Semicarbazone

Nasry Jassim Hussien^{a,b}, Yang Farina^a and
Mohamad Jaber Al-Jeboori^c

^a*School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor*

^b*Dept. of Chemistry, College of Education for Pure Science, Diyala University, Baqubah, Iraq*

^c*Dept. of Chemistry, College of Education (Ibn Al-Haitham), Baghdad University, Baghdad, Iraq*

Abstract. The diorganotin(IV) complexes of the type Me₂SnL, Bu₂SnL and Ph₂SnL (L) with the anion of the semicarbazone ligand formed by condensation reaction of 3,4-dihydroxybenzaldehyde with semicarbazide were synthesized using 1:1 metal to ligand reactant ratios. The newly synthesized complexes were characterized using elemental analysis, infrared and nuclear magnetic resonance (¹H, ¹³C, ¹¹⁹Sn) spectroscopic techniques. Complex formation between the organotin(IV) moiety and the anion of 3,4-dihydroxybenzaldehydesemicarbazone occurred with chelation at the *o*-dihydroxy positions. The complexes were proposed to have tetrahedral geometry.

Keywords: Synthesis, Semicarbazone, Diorganotin, Schiff base, Catechol

INTRODUCTION

The studies of organotin(IV) compounds have gained interest due to their various industrial and biocidal applications [1–5]. The organotin(IV) compounds have been actively studied because of versatile chemistry and potential as biologically active compounds. Among these compounds, the chemistry of organotin(IV) complexes of Schiff bases has been extensively studied due to its structural diversity, thermal stability, and the compounds have been proposed to possess mild-to-good antitumor [6–9], antimicrobial [10,11], antifungal [12–14], antibacterial [12–14], antioxidant [15] or anti-inflammatory properties [15,16]. However, the mode of biological activities of the organotin(IV) compounds is not completely known. The structure of the organotin(IV) complexes, coordination number, the extent of alkylation and the nature of the organic groups attached factors deciding the biological activities of the tin complexes [10,17,18]. Semicarbazone is a versatile ligand in both neutral and anionic forms [17]. Chelates of organotin(IV) moieties with N, O donor ligands [16,18] have received much attention during the last few years. Catechol is the conjugate acid of a chelating agent used widely in coordination chemistry. Catechol, also known as pyrocatechol or 1,2-dihydroxybenzene, is an organic compound with the molecular formula C₆H₄(OH)₂, it is the ortho isomer of the three isomeric benzenediols. The complexes formed between these catecholate types of semicarbazones have not been fully studied. This paper will describe the preparation and characterization of organotin(IV) complexes of catecholate semicarbazones.

EXPERIMENTAL DETAILS

Materials

All the following compounds were purchased from various sources as given in parentheses; semicarbazide (Fluka), 3,4-dihydroxybenzaldehyde (Aldrich), dimethylstannum (IV) dichloride (Aldrich), Dibutylstannum (IV) dichloride (Aldrich), diphenylstannum (IV) dichloride (Aldrich), ethanol (Fluka) and dimethyl sulfoxide (Merk). The compounds were used without further purification.

Synthesis

The ligand (H_2L) was produced by condensation of 3,4-dihydroxybenzaldehyde with semicarbazide [29]. The solid product which separated upon cooling were filtered and washed with ethanol. An outline of the reaction scheme is given in FIGURE 1.

Organostannum complexes of the ligand were produced by condensation of diorganotin (IV) dichloride with the ligand (H_2L) in the suitable solvents. The coloured solutions obtained were evaporated until the sediments appeared, which were filtered and washed with ethanol. The solid products were dried overnight in a vacuum desiccator over silica gel. An outline of the reaction scheme is given in FIGURE 2.

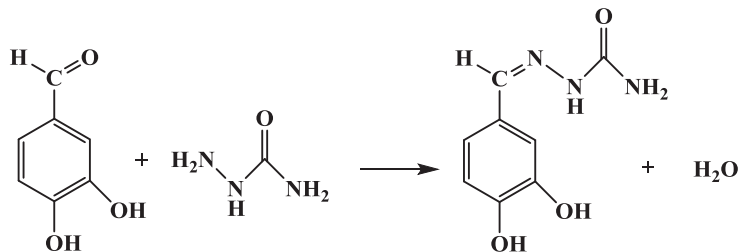


FIGURE 1. Reaction scheme for the synthesis of ligand

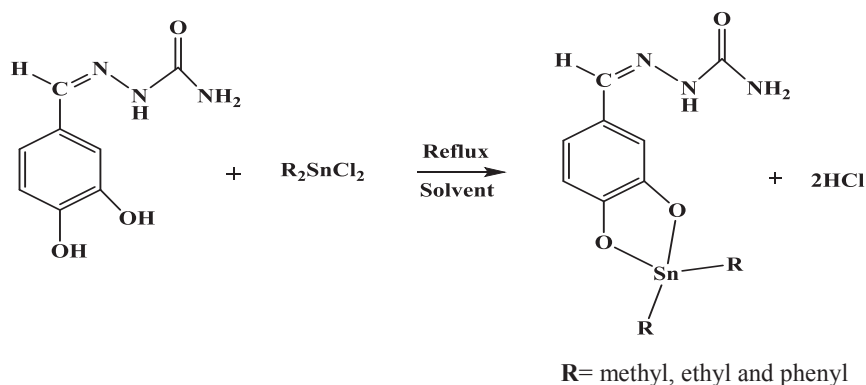


FIGURE 2. Reaction scheme for the synthesis of complexes

RESULT AND DISCUSSION

The ligand (H_2L) was prepared by condensation of 3,4-dihydroxybenzaldehyde with semicarbazide and was isolated as yellow solids. All the complexes are coloured solids. Elemental analysis and physical properties of the compounds are given in TABLE 1.

The IR wavenumbers of the ligand FIGURE 3 and the complexes FIGURE 4 are tabulated in TABLE 2. The azomethine $\nu(C=N)$ bands observed at $(1666 - 1664) \text{ cm}^{-1}$ for the complexes is similar to this appearing in the free ligand 1610 thus inferring that the nitrogen atom is not involved in bond formation with tin. The infrared spectra of the complexes in general showed strong bands centred around 1270 cm^{-1} which, may be attributed to $\nu(C-O)$. The $\nu(C-O)$ in the free ligand appeared at high wavenumber (1286) and similar trend has been reported [19]. The disappearance of the $\nu(O-H)$ found around 3380 cm^{-1} in the free ligand from the spectra of the complexes clearly indicated the double deprotonation of the ligand and the involvement of phenolic oxygens in chelate formation with the tin centers as reported by others [20-22]. The appearance of the new bands at 550 and 450 cm^{-1} in the spectra of the complexes may be assigned to $\nu(Sn-O)$ and $\nu(Sn-C)$ respectively and reaffirms the suggestion that the dialkyltin(IV) moieties are chelated to the oxygen atoms from the *o*-dihydroxy groups. Such a phenomenon has been reported [23].

TABLE 1. Analytical data and physical properties of the compounds

Compound	Color	Yield%	M. P. (°C)	Actual (Calcd.)%		
				C	H	N
H ₂ L	Yellow	85	215.2-216.5	48.83(49.23)	4.83(4.65)	22.1 (21.53)
Me ₂ SnL	Yellow	87	237.1-238.8	34.96(35.13)	4.12(3.83)	13.15(12.29)
Bu ₂ SnL	Red	84	235.7-237.8	44.87(45.10)	5.78(5.91)	10.76(9.86)
Ph ₂ SnL	Red	75	190.3-192.1	51.13(51.54)	3.85(3.68)	10.39(9.02)

TABLE 2. Important infrared wavenumbers of the ligand and complexes (cm⁻¹)

Compound	$\nu(\text{OH})$	$\nu[\text{N}(4)\text{H}]$	$\nu[\text{N}(2)\text{H}]$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{Sn}-\text{O})$	$\nu(\text{Sn}-\text{C})$
H ₂ L	3380	3267, 3182	3174	1610	1574	1286	-	-
Me ₂ SnL	-	3421, 3341	3210	1664	1582	1261	522	451
Bu ₂ SnL	-	3400, 3353	3265	1663	1549	1275	563	472
Ph ₂ SnL	-	3424, 3377	3114	1666	1524	1280	503	415

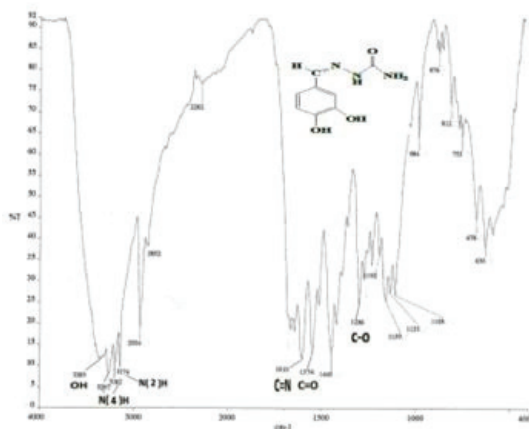


FIGURE 3. I.R spectrum of ligand (H₂L)

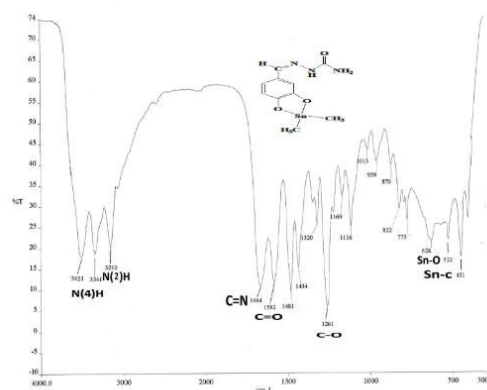


FIGURE 4. I.R spectrum of complex (Me₂SnL)

The ¹H NMR spectra for all compounds were recorded in [²H₆] DMSO using tetramethylsilane as the internal standard. The data are compiled in TABLE 3 while the numbering scheme for the carbon nuclei for the catechol Schiff base ligand and diorganotin (IV) catechol complexes are shown in FIGURE 5. Ligand H₂L FIGURE 6 gave a single resonance at δ 10.01 ppm attributable to the N(2)-H proton that is observed for semicarbazone derivatives. This peak was observed in low field due to hydrogen bonding with *d*₆-DMSO [24]. The spectrum also exhibit one singlet –OH peak at 9.04 due to the *o*-dihydroxy group. The hydroxy resonances is absent in the spectra of the complexes indicating double deprotonation and coordination of tin to the phenolic oxygens FIGURE 7. There is a small upfield shift of the aromatic protons resonances of the ligand upon chelation with the diorganotin(IV) moiety. The same effect has been reported [25]. These shifts may be attributed to a decrease in the electron density of the catechol ring due to electron withdrawing ability of the organotin(IV), which in turn decrease the ring current and deshielding of the ring protons. The complex R₂SnL show additional signals at δ 0.72, 0.8, 1.3, 1.5, 7.38 and 7.7 ppm due to the protons of alkyl and aryl groups, respectively.

TABLE 3. ¹H NMR spectra data (δ, ppm) of the ligand and complexes

Compound	-N(2)H	-N(4)H	-OH	-HC=N	Aromatic	Aliphatic
H ₂ L	10.01(1H)	6.33(2H)	9.04(2H)	7.66(1H)	7.30(1H), 6.92(1H), 6.73(1H)	-
Me ₂ SnL	10.3(1H)	6.7 (2H)	-	7.61(1H)	7.30(1H), 6.5(1H), 6.3(1H)	0.72(6H)
Bu ₂ SnL	10.45(1H)	6.83(2H)	-	7.5(1H)	7.2(1H), 6.4(1H), 6.2(1H)	1.5(4H), 1.3(8H), 0.8(6H)
Ph ₂ SnL	10.4(1H)	6.9(2H)	-	7.6(1H)	7.4(4H), 7.35(6H), 7.1(1H), 6.58(1H), 6.4(1H)	

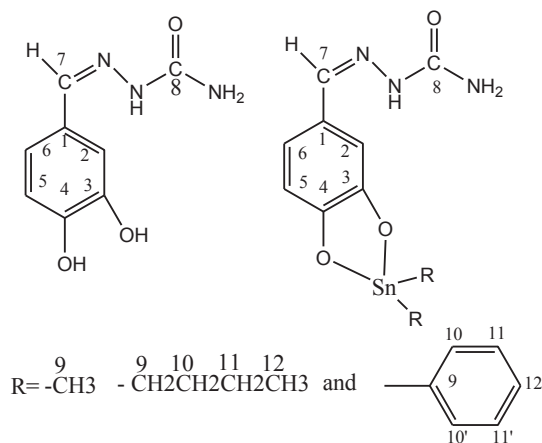


FIGURE 5. Catechol Schiff base ligand and catechol complexes showing the atom numbering scheme

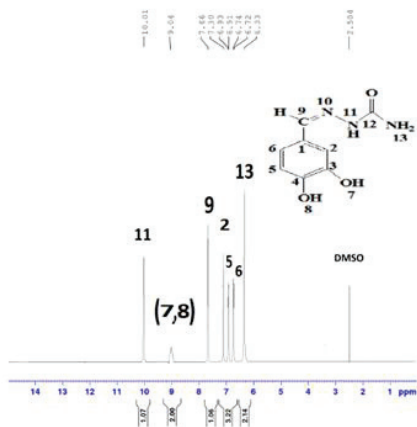


FIGURE 6. ¹H NMR spectrum of ligand (H₂L)



FIGURE 7. ¹H NMR spectrum of complex (Me₂SnL)

The ¹³C NMR for the ligand FIGURE 8 and complexes FIGURE 9 were recorded in [²H₆] DMSO. The spectrum of complexes show that upon complexation with the organotin(IV), the C-3 and C-4 nuclei resonances of the catecholate anion are shifted downfield compare to the ligand. Thus shifts could be attributed to decrease electron density at the carbon atoms when the oxygen is bounded to a metal ion [26]. This observation lends further evidence that the complexation occurred through the phenolic oxygen atoms, as shown in FIGURE 5.

¹¹⁹Sn NMR for the complexes FIGURE 10 were recorded in [²H₆] DMSO. Dimethyltin(IV) and dibutyltin(IV) complexes gave resonances at -120 and -135 ppm respectively which is well within the range for four-coordinated complexes [27]. In diphenyltin(IV) complex the ¹¹⁹Sn resonance appear at lower field region than dimethyltin(IV) and dibutyltin(IV), although of the greater electron withdrawing capability of the phenyl group. The resonance at δ (-450 ppm), probably reflects the greater shielding ability of the phenyl group, same co-

ordination number as reported by [28]. TABLE 4 shows the most relevant ^{13}C and ^{119}Sn NMR data.

TABLE 4. ^{13}C and ^{119}Sn NMR (δ , ppm) of the ligand and complexes

Compound	C=O	C-O	C=N	Aromatic	Aliphatic	^{119}Sn
H ₂ L	157.33	147.36	140.59	126.72, 119.56, 115.91, 113.57	-	-
Me ₂ SnL	157.11	147.72	145.91	120.12, 117.56, 114.91, 112.11	7.11(2C)	-120
Bu ₂ SnL	157.72	147.4	142.19	123,115,113,112	30.11, 25.11, 22.72, 15	-135
Ph ₂ SnL	157.68	147.68	145.86	142(4C), 135(2C), 127(6C), 119, 117, 114, 112	-	-450

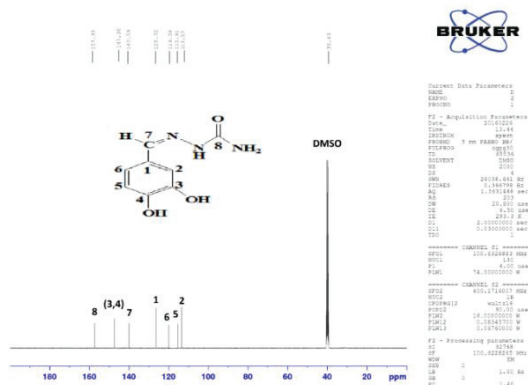


FIGURE 8. ^{13}C NMR spectrum of ligand (H₂L)

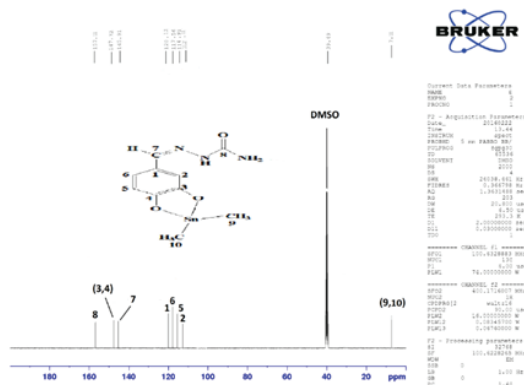


FIGURE 9. ^{13}C NMR spectrum of complex (Me₂SnL)

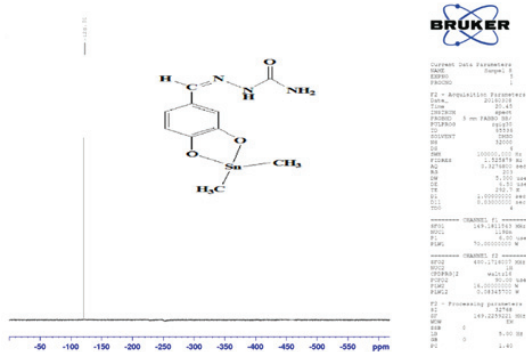


FIGURE 10. ^{119}Sn NMR of complex (Me₂SnL)

CONCLUSION

The ligand 3,4-dihydroxybenzaldehydesemicarbazone(H₂L) was synthesized by condensation method. The ligand were treated to various diorganotin(IV) chlorides to afford the corresponding complexes and water as the side product. The ligand coordinating through both the phenolic oxygens to the tin atom and the structural of the complexes are proposed to have tetrahedral geometry.

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