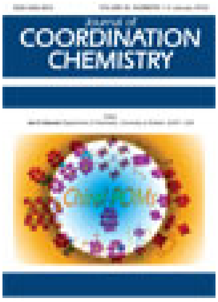

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Homobimetallic complexes containing Sn(IV) with acetylene dicarboxylic acid: their syntheses and structural interpretation by spectroscopic, semi-empirical, and DFT techniques

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Homobimetallic complexes containing Sn(IV) with acetylene dicarboxylic acid: their syntheses and structural interpretation by spectroscopic, semi-empirical, and DFT techniques

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Homobimetallic carboxylates with general formulae $(R_3Sn)_2L$ (where R = Me, *n*-Bu, Ph and L = acetylene dicarboxylate dianion) have been synthesized by refluxing disodium salt of acetylene dicarboxylic acid with triorganotin chlorides in 1 : 2 (L : M) molar ratio in methanol under reflux. These complexes have been characterized by elemental analyses, FTIR, and multinuclear NMR (^1H, ^{13}C) spectroscopies. DFT calculations have been performed for structural elucidation and results were compared with semi-empirical data. FTIR data indicate bidentate chelation of the ligand with tin and the complexes exhibit five-coordinate geometry in the solid state. Such coordination behavior is also supported by DFT and semi-empirical studies. NMR data confirm four-coordinate geometry in solution.

Keywords: Homobimetallic complexes; Spectroscopy; Semi-empirical study; DFT

1. Introduction

Organotin complexes have been found to be important in various fields [1], effective catalysts [2, 3], PVC stabilizers [4], and have also contributed an important role as fungicides, bactericides, and wood preservatives [5–7]. Some of them possess very promising *in vitro* antitumor properties against human tumor cell lines [8–10]. The study of organotin carboxylates is important and interesting in that their biological activity may also be affected by the structure of the molecule as well as coordination behavior of tin [11, 12]. Combination of two biologically active entities in the same molecule could enhance their activity [13]. Detailed studies of syntheses, characterizations, and biological applications of organotin carboxylates are of interest [14–16]. In continuation

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$$HOOC—C{\equiv}C—COOH$$

Figure 1. Acetylene dicarboxylic acid **H_2L**.

of our previous work [17–19], we report here the synthesis, characterization, DFT, and semi-empirical study of homobimetallic complexes containing Sn(IV) with acetylene dicarboxylic acid (figure 1).

2. Experimental

2.1. *Materials and methods*

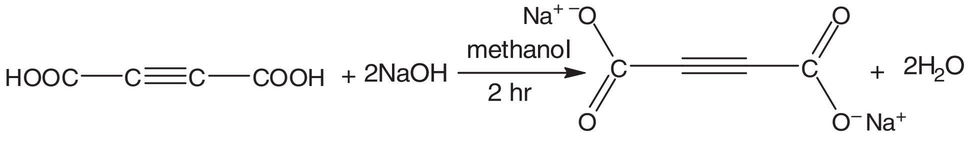
Trimethyl-, tributyl-, and triphenyltin chlorides and sodium hydroxide were purchased from Aldrich (Germany) and used without purification. Acetylene dicarboxylic acid was of Merck (Germany) origin. The solvents were dried by reported procedures [20]. Melting points were noted by taking the samples in capillary tubes using the electrochemical melting point apparatus model MP-D Mitamura Rikero Kogyo (Japan) and are uncorrected. Elemental analyses were performed on a CHN-932 elemental analyzer, Leco Corporation, USA. Infrared (IR) spectra were recorded by a Perkin-Elmer-1000 FTIR spectrophotometer from 4000 to 400 cm $^{-1}$. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARC 300 MHz-FT-NMR spectrometer.

DFT calculations were performed in the gas phase using the Firefly QC package [21], which is partially based on the GAMESS (US) [22] source code using the BLYP exchange-correlation functional [23, 24] and the 3-21 G basis set [25]. BLYP is a pure DFT method that combines Becke's 1988 exchange functional [26] with the correlation functional of Lee–Yang–Parr [24].

The semi-empirical studies were done by MOPAC 2007 [27] program in the gas phase using the PM3 method [26, 28]. Selected parts of the complexes not containing the metal ion were preoptimized using molecular mechanics methods. Several cycles of energy minimization had to be carried for each molecule. Geometry was optimized using Eigen Vector. The root mean square gradient for molecules was all less than one. Self-consistent field was achieved in each case. Absences of imaginary frequencies were checked to confirm the global minimum in both methods.

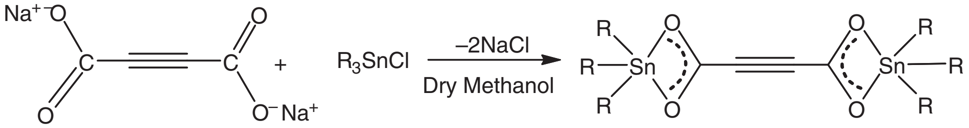
2.2. *Synthesis of the sodium salt of acetylene dicarboxylic acid (Na_2L)*

Sodium hydroxide (20 mmol) was suspended in 50 mL methanol in a round bottom flask followed by dropwise addition of methanolic solution (20 mL) of acetylene dicarboxylic acid (10 mmol) at room temperature. The reaction mixture was continuously stirred for 2 h. The solvent was evaporated through the rotary evaporator under reduced pressure. The solid mass left behind was dried in open air.



2.3. *General procedure for synthesis of 1–3*

To a solution of R_3SnCl (2 mmol) in 60 mL dry methanol in a quickfit two necked 250 mL round bottom flask, sodium salt of acetylene dicarboxylic acid (1 mmol) was added in portions with continuous stirring, and the reaction mixture was refluxed for 10 h. The precipitated sodium chloride was removed by filtration and the solvent was evaporated slowly at room temperature. The solid product obtained was recrystallized in methanol : *n*-hexane (5 : 1).



where R = Me **1**, *n*-Bu **2**, Ph **3**.

3. Results and discussion

All the complexes have sharp melting points and are soluble in DMSO solvent only. The physical data of the synthesized complexes **1**–**3** are given in table 1.

3.1. *IR spectroscopy*

IR spectra of the free ligand and complexes were recorded from 4000 to 400 cm^{-1}; important vibrational bands in the complexes are summarized in table 2.

Table 1. Physical data of homobimetallic complexes of acetylene dicarboxylate.

Compound No.	Molecular formula	Molecular weight	Yield (%)	m.p. (°C)	Elemental analysis % Calcd/found C	Elemental analysis % Calcd/found H
Na$_2$L	$C_4O_4Na_2$	158.04	96	> 349	30.37/30.33	–
1	$C_{10}O_4H_{18}Sn_2$	439.57	85	190–191	27.30/27.34	4.13/4.10
2	$C_{28}O_4H_{54}Sn_2$	692.04	93	185–186	48.55/48.59	7.86/7.90
3	$C_{40}O_4H_{30}Sn_2$	810.96	89	90–92	59.19/59.23	3.73/3.77

Table 2. IR data (cm^{-1}) of homobimetallic complexes of acetylene dicarboxylate.

Compound No.	νC≡C	νCOO_{asym}	νCOO_{sym}	$\Delta\nu$	νSn–C	νSn–O
Na$_2$L	2240 m	1715 s	1428 s	288	–	–
1	2210 m	1564 s	1443 m	121	547 s	482 s
2	2207 m	1572 s	1443 m	129	513 s	432 s
3	2212 m	1551 s	1439 m	112	–	445 s

s, strong; m, medium.

The bonding mode of metal carboxylates can be found from the differences ($\Delta\nu = \nu CO_{2(asym)} - \nu CO_{2(sym)}$) between asymmetric and symmetric carboxylate stretching frequencies. According to the literature [29], if $\Delta\nu > 200$–$260\,cm^{-1}$, unidentate coordination is indicated while $\Delta\nu < 200\,cm^{-1}$ indicates bidentate mode. Between the two extremes, there exists anisobidentate mode where one metal oxygen contact is significantly shorter than the other. For the sodium salt of ligand, $\Delta\nu$(COO) is $288\,cm^{-1}$, indicating unidentate bonding. The $\Delta\nu$(COO) of complexes lies in the range 129–$112\,cm^{-1}$ due to bidentate coordination of carboxylate to triorganotin [30]. Absorptions at 482–$432\,cm^{-1}$ were assigned to Sn–O bond [17, 31]. The absence of Sn–O band in the precursor and the presence in the complexes confirms the coordination to tin(IV) from the carboxylate oxygen atoms [32], which is direct evidence for complexation.

3.2. *^{1}H NMR spectroscopy*

The spectra of the complexes were recorded in deuterated DMSO. The numbers of protons calculated by the integration of the peaks are in very good agreement to those theoretically calculated by incremental method [33]. The free ligand has a singlet at 12.2 ppm for the −OH proton of carboxylic acid group. The absence of this signal and appearance of new signals in the expected range for the organotin moieties are evidence for complex formation. The ^{1}H NMR chemical shift values (ppm) of the complexes are given in table 3.

The methyl protons in **1** appear as a singlet at 0.55 ppm. As far as **2** is concerned, the chemical shifts at 1.07 and 0.86 ppm were assigned to the α-methylene and terminal methyl moieties, respectively, for *n*-butyl group. Both give very clear triplets due to the coupling of α-methylene protons with two protons of the adjacent β-methylene and the protons of terminal methyl group couple with the two γ-methylene protons in close vicinity. The two multiplets at 1.54–1.60 ppm and 1.23–1.35 ppm arise due to protons at β- and γ-positions, respectively. The ^{1}H NMR spectrum of **3** exhibits three sets of signals in the downfield region, i.e., a doublet at 7.95 ppm for ortho protons, a multiplet at 7.83–7.90 ppm for meta protons, and a multiplet at 7.38–7.43 for para protons [18].

3.3. *^{13}C NMR spectroscopy*

^{13}C NMR spectra were recorded in DMSO and data are given in table 4. Acetylenic carbons b,′b give signal at 75.64–75.99 ppm in **1**–**3** suggesting that alkyne does not participate in coordination. The signals at 158.35–156.09 ppm are caused by carbons (a,′a) of the coordinated carboxylate. The a,′a carbons show downfield shift in the complexes as compared to parent acid, indicating coordination of carboxylate

Table 3. ^{1}H NMR data of homobimetallic complexes of acetylene dicarboxylate.

Compound No.	Chemical shifts (ppm)
1	$Sn–CH_3 = 0.55$ s $^2J[77]$
2	$Sn–CH_2–CH_2–CH_2–CH_3 = 1.07$ t, 1.54–1.60 m, 1.23–1.35 m, 0.86 t (7.0)
3	$Sn–C_6H_5 = 7.95$ d, 7.83–90 m, 7.38–7.43 m

to tin(IV) [34]. The chemical shift for carbon of methyl, *n*-butyl and phenyl groups attached to tin are almost observed at the same positions as predicted from the literature [35, 36]. The $^nJ(^{119}Sn–^{13}C)$ coupling for **1** and **2** are 378 and 578 Hz, respectively, which is indicative of four-coordinate geometry [37] in solution. The C–Sn–C bond angles in **1** and **2** are 109.9° and 127.5° (table 5) as calculated by Lockhart equation [38].

3.4. *DFT calculations and semi-empirical study*

Complexes **1** and **3** have symmetrical computed structures as shown in figures 2 and 3, respectively. The bond angles and bond lengths are all typical of organotin compounds. In the structure obtained by DFT for **1**, the angle between the planes of two carboxylates (Sn9–O8–C7–O22) and (Sn1–O2–C3–O4) is 81.5°, while in **3** similar planes (Sn1–O4–C3–O2) and (Sn9–O8–C7–O43) make an angle of 77.04° with each other. In the structure obtained by semi-empirical PM3 method for **1**, the planes between the two carboxylate groups (Sn9–O8–C7–O22) and (Sn1–O2–C3–O4) is 89.4°, while in **3** similar planes (Sn1–O4–C3–O2) and (Sn9–O8–C7–O43) make an angle of 89.8° with each other. The carboxylate oxygen (with the short C–O bond) is bound to tin with a longer Sn–O bond while the other carboxylate oxygen (with the long C–O bond) is bound to tin with a shorter Sn–O bond. This asymmetric coordination behavior is documented in X-ray crystal structures of organotin carboxylates [39]. Semi-empirical study yields slightly shorter Sn–O bond lengths and slightly lesser O–Sn–O bond angles than those obtained by DFT techniques. The selected bond angles and bond lengths of both complexes are tabulated in tables 6 and 7, respectively.

Table 4. ^{13}C NMR data of homobimetallic complexes of acetylene dicarboxylate.

Compound No.	a, ′a	b, ′b
H_2L/Na_2L	154.08	75.69
1	158.47	75.64
2	156.33	75.97
3	156.09	75.97

1: Sn–CH_3, (C–α)– 1.87 ^1J[378]. **2**: Sn–$CH_2CH_2CH_2CH_3$, (C–α) 19.33 ^1J[578], (C–β) 28.05 ^2J[33], (C–γ) 26.92 ^3J[86], (C–δ) 14.03. **3**: Sn–C_6H_5, (C–α) 136.75 ^1J[638], (C–β) 129.36 ^2J[47], (C–γ) 128.47, (C–δ) 128.00.

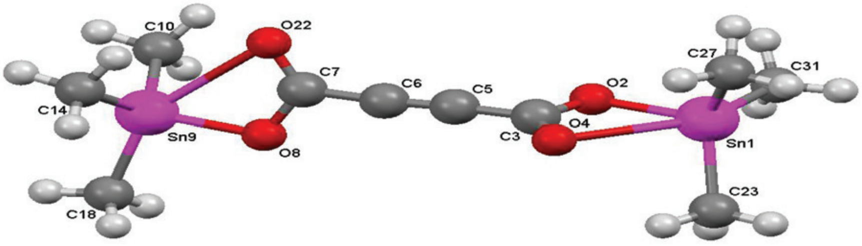


Figure 2. BLYP 3-21 G geometry optimized structure of **1**.

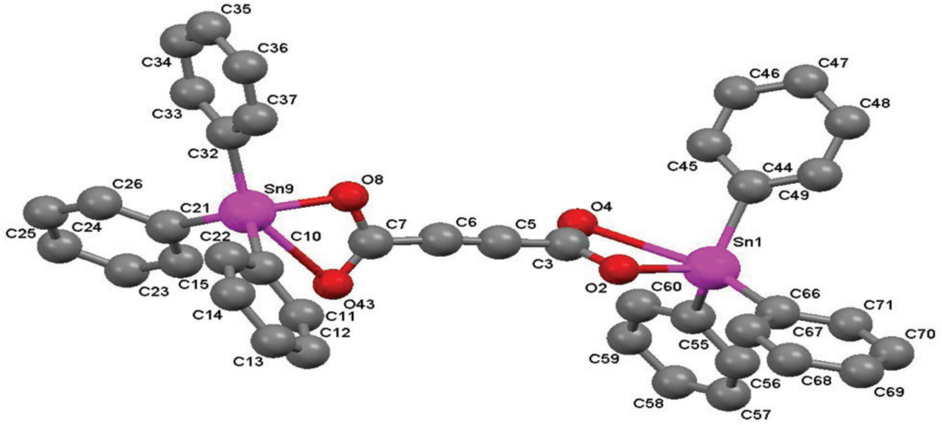


Figure 3. BLYP 3-21 G geometry optimized structure of 3 (all hydrogen atoms are omitted for clarity).

Table 5. C–Sn–C angles (°) calculated from NMR.

Compound No.	${}^{1}J[{}^{119}\text{Sn}–{}^{13}\text{C}]$ (Hz)	C–Sn–C angles (°) calculated
1	378	109.9
2	578	127.5

Table 6. Selected bond angles (°) of homobimetallic complexes of acetylene dicarboxylate.

Bond angle (°)	Compound **1**		Compound **3**	
	BLYP/3-21 G	PM3	BLYP/3-21 G	PM3
O–Sn–O	O2–Sn1–O4		O4–Sn1–O2	
	51.78	49.63	53.21	49.27
	O8–Sn9–O22		O8–Sn9–O43	
	51.76	49.63	52.67	47.93
O–C–O	O4–C3–O2		O4–C3–O2	
	122.75	112.4	121.93	112.43
	O8–C7–O22		O8–C7–O43	
	122.76	112.4	122.01	113.23
O–C–C	O4–C3–C5		O4–C3–C5	
	123.75	128	123.46	128.12
	O2–C3–C5		O2–C3–C5	
	113.49	119.59	114.6	119.45
	O8–C7–C6		O8–C7–C6	
	113.47	119.59	115.43	119.12
	O22–C7–C6		O43–C7–C6	
	123.76	128.0	122.56	127.66
C–C–C	C3–C5–C6		C3–C5–C6	
	175.93	179.6	176.74	179.6
	C7–C6–C5		C7–C6–C5	
	175.97	179.6	174.34	179.55

Table 7. Selected bond lengths (Å) of homobimetallic complexes of acetylene dicarboxylate.

	Compound **1**			Compound **3**		
Bond length (Å)		BLYP/ 3-21 G	PM3		BLYP/ 3-21 G	PM3
O–Sn	Sn9–O8	2.10	2.02	Sn9–O8	2.12	2.01
	Sn1–O2	2.10	2.02	Sn1–O2	2.11	2.01
	Sn9–O22	2.91	2.77	Sn9–O43	2.84	2.87
	Sn1–O4	2.91	2.77	Sn1–O4	2.82	2.79
O–C	C7–O8	1.36	1.32	C7–O43	1.27	1.23
	C3–O2	1.36	1.32	C3–O4	1.27	1.23
	C7–O22	1.26	1.23	C7–O8	1.35	1.32
	C3–O4	1.26	1.24	C3–O2	1.35	1.32
C≡C	C5–C6	1.22	1.19	C6–C5	1.22	1.19
≡C–COO–	C7–C6	1.44	1.44	C7–C6	1.44	1.44
	C3–C5	1.44	1.44	C3–C5	1.44	1.44

4. Conclusion

FTIR data of the complexes indicate that both the oxygen atoms of the dicarboxylate chelate tin in a bidentate mode. This type of coordination behavior is also confirmed by DFT calculations and semi-empirical study. All complexes have five-coordinate geometry in the solid state and four-coordinate geometry in solution. The bond lengths (Sn–O) and bond angles (O–Sn–O) calculated by semi-empirical studies for **1** and **3** are slightly shorter than those obtained by DFT calculations.

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