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Synthesis, crystal structure, and fungicidal activity of triorganotin(IV) 1-methyl-1*H*-imidazole-4-carboxylates

Abstract: Two triorganotin carboxylates of 1-methyl-1*H*-imidazole-4-carboxylic acid (HL), Cy_3SnL and $C_6H_5C(CH3)_2CH_2SnL$, have been prepared by the reaction of the ligand with tricyclohexyltin hydroxide and fenbutatin oxide, respectively. The complexes were characterized by ^{1}H NMR, infrared, and elemental analysis. The molecular structure of complex **1** was determined by using a single-crystal X-ray diffraction analysis. Preliminary bioassay indicated complex **1** exhibiting good and broad-spectrum fungicidal activities.

Keywords: crystal structure; fungicidal activity; 1-methyl-1*H*-imidazole-4-carboxylic acid; organotin(IV) carboxylates.

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Introduction

In recent years, organotin carboxylates have attracted interest because of their versatile molecular structures, such as monomers (Dong et al., 2014), dimers (Liu et al., 2011), tetramers (Ndoye et al., 2013), oligomers, and polymers (Garcia-Zarracino and Hopfl, 2005; Seter et al., 2012). Organotin carboxylates possess a wide range of applications such as biological properties (Kaur et al., 2013; Carraher and Roner, 2014), coatings, and catalysis and serve as additives to polymers (Hadjikakou and Hadjiliadis, 2009; Baul et al., 2012). Some organotin compounds can also be used as pesticides, for example, azocyclotin and fenbutatin oxide (Damotter and Collot, 1982), which are both excellent acaricides. Imidazole is one of the heterocycles containing nitrogen with many kinds of bioactivities, such as anticancer, antifungal, antineuropathic, antihistaminic, and antibacterial activities (Rani et al., 2013; Zhang et al., 2014). However, the toxicity and resistance of some organotin pesticides have seriously reduced their efficiency (Wearing et al., 2014). To develop novel organotin pesticides with a wide spectrum of biological activities and lower toxicity, a series of novel organotin derivatives of 1-methyl-1-methyl-1*H*-imidazole-4-carboxylic acid was designed and synthesized. In this study, the fungicidal activities of the target complexes against nine fungi were evaluated systematically.

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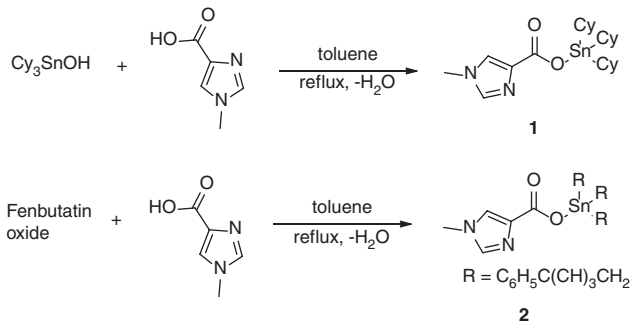
Results and discussion

Syntheses

The triorganotin carboxylates **1** and **2** have been prepared by the reaction of 1-methyl-1*H*-imidazole-4-carboxylic acid (HL) with tricyclohexyltin hydroxide and fenbutatin oxide, respectively, in an appropriate mole ratio in dry toluene (Scheme 1).

Infrared spectra

The characteristic infrared (IR) bands of the two complexes have been identified by comparing the data with similar organotin compounds. IR stretching frequencies of the carboxylate group (COO) have been used to distinguish coordinated from noncoordinated carboxyl groups and to determine the mode of coordination of the carboxylate ligand to the tin atom. The ν_{as}(COO) and ν_s(COO) bands appear at 1585 and 1435 cm^{-1} for sodium 1-methyl-1*H*-imidazole-4-carboxylate. However, the ν_{as}(COO) and ν_s(COO) bands appear at 1645 and 1391 cm^{-1} for complex **1**; the $\Delta\nu[\nu_{as}(COO)\text{-}\nu_s(COO)]$ is 254 cm^{-1}, which is significantly larger than that observed for the sodium salt of the ligand



Scheme 1: Synthesis route for the complexes **1** and **2**.

($\Delta\nu[\nu_{as}(COO)\text{-}\nu_{s}(COO)]$=150 cm^{-1}), indicating that the carboxylic group takes a unidentate coordination mode to the Sn atom in complex **1** (Szorcsik et al., 2004). Similarly, in complex **2**, the carboxylic group also takes a unidentate coordination mode because of a $\Delta\nu[\nu_{as}(COO)\text{-}\nu_{s}(COO)]$ of 275 cm^{-1} for complex **2**.

^{1}H NMR spectra

In the ^{1}H NMR spectra of all the complexes, the total number of proton resonances is in agreement with the expected molecular composition. The methyl protons connected to the imidazole ring resonate as singlets in the expected range of 3.72 ppm. The protons of the imidazole ring resonate as a singlet in the expected range of 7.0–7.5 ppm in different complexes.

Crystal structure of complex 1

The molecular structure of complex **1** is shown in Figure 1, and the selected bond lengths and angles are listed in Table 1. As shown in Figure 1, the coordination geometry about Sn is a distorted tetrahedron, in which three carbon atoms of the cyclohexyl groups and one oxygen atom of the carboxylic group occupy the vertexes. The Sn(1)-O(1) distance of 2.077(3) Å indicates a strong bond between these atoms. The Sn(1)-O(2) distance of 2.818(3) Å is larger than the sum of the covalent radii of Sn and O (2.14 Å). However, it is shorter than the sum of the van der Waals radii of Sn and O (3.70 Å), indicating the existence of weak contacts between Sn(1) and O(2). Owing to this intramolecular Sn→O interaction, the coordination geometry distorts from the ideal tetrahedron, and the tin atom can be interpreted as being [4+1] coordinated. The distortion from ideal tetrahedral geometry is also expressed by the O(1)-Sn(1)-C(11) [92.83(12)°], O(1)-Sn(1)-C(6) [107.11(15)°], and O(1)-Sn(1)-C(18) [112.95(12)°] angles.

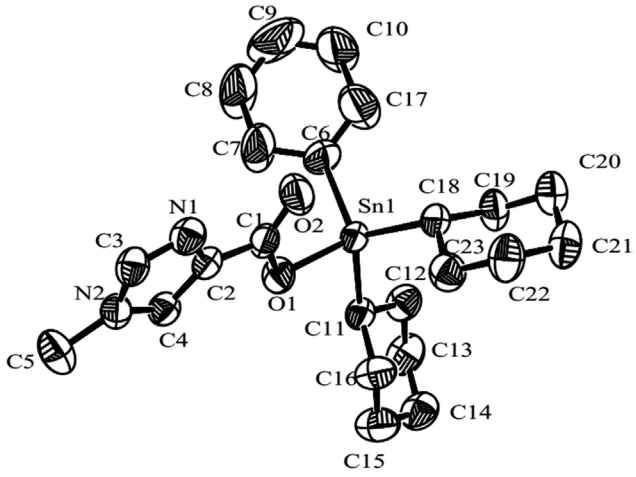


Figure 1: Molecular structure of complex **1** (ellipsoids at 30% probability; hydrogen atoms are omitted for clarity).

Table 1: Selected bond lengths (Å) and angles (°) for complex **1**.

Bond lengths	Å	Angles	°
Sn(1)-O(1)	2.077(3)	O(1)-Sn(1)-C(18)	112.95(12)
Sn(1)-O(2)	2.818(3)	O(1)-Sn(1)-C(6)	107.11(15)
Sn(1)-C(6)	2.165(4)	C(18)-Sn(1)-C(6)	113.50(18)
Sn(1)-C(18)	2.170(4)	C(18)-Sn(1)-C(11)	116.38(14)
Sn(1)-C(11)	2.170(5)	O(1)-Sn(1)-C(11)	92.83(12)
C(1)-O(2)	1.206(5)	C(6)-Sn(1)-C(11)	111.98(19)
C(1)-O(1)	1.337(5)	O(2)-C(1)-O(1)	121.5(3)
C(1)-C(2)	1.463(5)	O(2)-C(1)-C(2)	124.9(4)
C(2)-C(4)	1.355(5)	O(1)-C(1)-C(2)	113.6(3)
C(2)-N(1)	1.384(4)	C(3)-N(2)-C4	106.3(3)
C(3)-N(1)	1.301(5)	C(4)-N(2)-C(5)	126.4(3)
C(3)-N(2)	1.345(5)	C(3)-N(2)-C(5)	127.2(3)
C(5)-N(2)	1.466(6)	C(4)-N(1)-C(5)	112.0(2)

Biological activity

The fungicidal activities of the title complexes against nine fungi, that is, *Alternaria solani* (AS), *Botrytis cinerea* (BC), *Cercospora arachidicola* (CA), *Gibberella zeae* (GZ), *Phytophthora infestans* (Mont.) de Bary (PI), *Physalospora piricola* (PP), *Pellicularia sasakii* (Shirai) (PS), *Sclerotinia sclerotiorum* (SS), and *Rhizoctonia cerealis* (RC), at the dosage of 50 μg/mL were measured according to the fungi growth inhibition method reported (Zuo et al., 2010), and data are shown in Table 2. The preliminary screening results indicated that all the title complexes have fungicidal activities in a certain degree. In contrast to complex **2** and the corresponding controls, complex **1** exhibits a broad spectrum of fungicidal activity against nine fungi with a growth inhibition no <40%. Complex **1** also presents very

Table 2: Growth inhibition rate of the title compound to different fungi (%) at 50 μg/mL.

Compound	AS	CA	GZ	PP	BC	SS	RC	PS	PI
1	40.0	55.0	79.7	87.7	58.0	72.4	88.9	88.1	61.9
2	43.3	40.0	76.7	50.8	29.0	82.7	16.6	55.9	19.0
Fenbutatin oxide	36.7	45.0	58.1	64.9	35.4	86.2	20.8	59.3	28.5
Carbendazim	20.0	5.0	97.6	94.7	25.8	100.0	87.5	98.3	90.4

good fungicidal activity against PP, RC, PS, with a growth inhibition of 87.7%, 88.9%, and 88.1%, respectively.

Conclusions

Two triorganotin carboxylates containing the imidazole ring have been synthesized from 1-methyl-1*H*-imidazole-4-carboxylic acid and the corresponding triorganotin hydroxide or triorganotin oxide, respectively. The carboxylate in the compounds is monodentate, and the tin atom possesses a distorted C_3SnO tetrahedral geometry. Compound **1** that has a good activity against nine fungi can be considered as antifungicidal compounds for further study.

Experimental

The melting points of all compounds were determined on an X-4 binocular microscope (Gongyi Tech. Instrument Co., Henan, China), and the thermometer was not corrected. IR spectra were recorded on a Nicolet 470 FT-IR spectrophotometer (Thermo Nicolet Corporation, Madison, WI, USA) using KBr discs in the range 4000–400 cm^{-1}. Proton NMR spectra were measured using a Bruker AC-P 400 spectrometer (Bruker Corporation, Switzerland), and chemical shift values (δ) were reported as parts per million, with tetramethylsilane as the internal standard. Elemental analyses were determined on a Yanaca CHN Corder MT-3 elemental analyzer (Elementar Corporation, Germany). The single-crystal structure for X-ray diffraction was performed with a Brucker Smart 1000 CCD diffractometer (Bruker Corporation, Switzerland). All solvents and liquid reagents (Energy Chemical Reagent Co., Ltd., Shanghai, China) were of analytical reagent grade and were dried in advance and distilled before use.

Synthetic procedure for complexes 1 and 2

Tricyclohexyltin hydroxide (2.0 mmol) or fenbutatin oxide (2.0 mmol) and 1-methyl-1*H*-imidazole-4-carboxylic acid (HL, 2.0 mmol) were heated at reflux for 12 h, under the azeotropic removal of H_2O using a Dean-Stark apparatus. After cooling down to room temperature, the solution was filtered. The solvent was removed *in vacuo* to give the crude complexes **1** and **2**, respectively. The compounds were purified by recrystallization from ethanol. The spectroscopic data are given as follows:

Complex 1: White solid. Yield: 81%, m.p. 112°C–114°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.28–1.35 (m, 9H), 1.63–1.72 (m, 15H), 1.95–1.98 (m, 9H), 3.72 (s, N-CH_3), 7.46 (s, 1H), 7.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.9, 28.9, 31.2, 33.7, 33.9, 125.7, 135.7, 138.2, 167.6. ^{119}Sn NMR (100 MHz, $CDCl_3$) δ: 11.2. Anal. Calcd. for $C_{23}H_{38}N_2O_2Sn$: C, 56.00; H, 7.76; N, 5.68. Found: C, 54.78; H, 7.55; N, 5.77. IR (KBr, cm^{-1}): IR (KBr, cm^{-1}): 1645 ν_{as}(COO), 1391 ν_s(COO), 681 (Sn-C), 543 ν(Sn-O).

Complex 2: White solid. Yield: 84%, m.p. 96°C–98°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.22 (s, 18H, CH_3), 1.24 (s, 6H), 3.72 (s, 3H, N-CH_3), 7.06–7.11 (m, 6H), 7.19–7.22 (m, 3H), 7.26–7.30 (m, 5H), 7.36–7.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 32.8, 33.6, 37.1, 33.8, 125.2, 125.4, 125.8, 128.3,136.6, 138.3, 151.1, 166.8. ^{119}Sn NMR (100 MHz, $CDCl_3$) δ: 88.6. Anal. Calcd. for $C_{35}H_{44}N_2O_2Sn$; C, 65.33; H, 6.89; N, 4.35; O, 4.97. Found: C, 65.11; H,6.26; N, 4.03. IR (KBr, cm^{-1}): 1677 ν_{as}(COO), 1403 ν_s(COO), 705 (Sn-C), 455 ν(Sn-O).

Crystal structure determination for complex 1

The crystal of complex **1** was grown from a mixture of *n*-hexane and ethyl acetate (2:1). X-ray intensity data were recorded on a Bruker SMART 1000 CCD diffractometer using graphite monochromated Mo-Kα radiation (λ=0.71073 Å). The structure was solved by direct methods with the SHELXS-97 program (Sheldrick, 1997). Refinements were performed using the full-matrix least squares on F^2 with SHELXL-97 (Sheldrick, 1997). All nonhydrogen atoms were refined with anisotropic temperature parameters. Hydrogen atoms were placed in a calculated position. A summary of the crystal data, experiment, and refinement is presented in Table 3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1013293.

Fungicide screening

Preliminary screening was conducted by using the fungi growth inhibition method of Zuo et al. (2010), using potato dextrose agar (PDA) as cultivation medium. A stock solution of each compound was prepared at 50 μg/mL using sterilized water containing 2 drops of *N*,*N*-dimethylformamide as a solvent, and then 1 mL of the stock solution was transferred into a 10-cm-diameter Petri dish. Nine milliliters of PDA was then added to prepare the plate containing 50 μg/mL of the test compound. Before the plate solidification, the PDA was thoroughly mixed by turning the Petri dish in the sterilized operation desk five times to evenly scatter the compound in PDA. Then a 4-mm diameter of the fungi cake was inoculated on the plate and cultured in the

Table 3: Crystal data and details of structure refinement parameters for complex **1**.

Complex	1
Empirical formula	$C_{23}H_{36}N_2O_2Sn$
Formula weight	491.23
T (K)	296(2)
Radiation (λ/Å)	0.71073
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions (Å and °)	a=10.933(6), b=13.269(7), c=16.398 (9); β=90
Volume (Å^3)	2379(2)
Z	4
Calculated density (g cm^{-3})	1.372
Absorption coefficient (mm^{-1})	1.093
F(000)	1016
Crystal size (mm)	0.32×0.26×0.21
Theta range (°)	2.41–27.82
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 15$, $-19 \le l \le 19$
Reflections collected	12094
Independent reflections	4186 [R(int)=0.0227]
Completeness to θ max.	100.0%
Maximum and minimum transmission	0.8023 and 0.7203
Observed data/restraints/parameters	4186/24/254
Goodness of fit on F^2	1.063
Final R indices [I>2sigma(I)]	R_1=0.0275; wR_2=0.0695
R indices (all data)	R_1=0.0290; wR_2=0.0703
Largest difference peak and hole (e$^-$ Å^{-3})	0.399 and -0.747

culture tank at 24°C to 26°C. The diameter of the fungi spread was measured 2 days later. Growth inhibition was then calculated using the corresponding control. Fungi used in this study included AS, BC, CA, GZ, PI, PP, PS, SS, and RC.

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