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Note

Synthesis and crystal structure of a new macrocyclic dimethyltin(IV) complex with 5-phenyl-1,3,4-oxadiazole-2-thiol linked by intermolecular C=S···O non-bonded weak interactions

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Abstract

A new macrocycle dimethyltin(IV) complex **1** has been synthesized by the reaction of 5-phenyl-1,3,4-oxadiazole-2-thiol with dimethyltin dichloride in the presence of sodium ethoxide. The complex **1** has been characterized by elemental, IR, ^{1}H, ^{13}C, ^{119}Sn NMR spectra and X-ray crystallography diffraction analyses. X-ray data reveal that a 24-membered macrocycle associated by intermolecular C=S···O non-bonded weak interactions. The geometry about each tin atom involved is distorted trigonal bipyramidal.

Keywords: 5-Phenyl-1,3,4-oxadiazole-2-thiol; Organotin(IV); Macrocycle; Crystal structure

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1. Introduction

In the past few years, metal-directed self-assembly has become a powerful tool for the construction of systems having cavities or possessing intrinsic physical and chemical properties that are promising for the creation of new materials and new metal-drugs [1]. More recently, the non-covalent weak molecular forces, which can connect these metallic subunits into the more intriguing and loose supramolecular infrastructures, have been widely investigated in structural chemistry, structural biology and the pharmaceutical sciences [2]. Intra- and intermolecular non-bonded S···X (X = O, S, N, etc.) interactions have been investigated for characterization of the molecular structures in a large number of organosulfur compounds [3]. These intra- and intermolecular non-bonded interactions seem to be very attractive from the viewpoint of the construction of a new molecular recognition system in chemical reactions [4] and medicinal biochemistry [5]. In all, non-bonded S···O [6], S···N [7], S···π [8] and S···S [9,10] interactions have all attracted particular interest.

Here, we report a new macrocycle complex linked by intermolecular C=S···O non-bonded weak interaction. By the reaction of 5-phenyl-1,3,4-oxadiazole-2-thiol and dimethyltin dichloride, in the presence of sodium ethoxide. Due to the hydrolysis of dimethyltin dichloride, we got a 24-membered macrocycle complex associated by intermolecular C=S···O non-bonded weak interactions. This work deals with the preparation and structural characterization of the complex.

2. Results and discussion

2.1. Synthesis aspects of complex 1

The complex **1** has been synthesized by the reaction of 5-phenyl-1,3,4-oxadiazole-2-thiol with dimethyltin dichloride in the presence of sodium ethoxide. A 24-membered was constructed macrocycle by intermolecular C=S···O non-

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bonded weak interactions. The reaction equation is shown in Scheme 1.

2.2. IR and NMR data

It is worthy to note that the absorption at 2550 cm^{-1} in free ligand owing to the –SH group is absent in the spectra of complex **1**. And new absorption in the region of Sn–S vibration observed in common organotin(IV) derivations of thiolate (300–400 cm^{-1}) which evidences the deprotonation of the mercapto group is not found [11,12]. But a new weak absorption appears at 486 cm^{-1} is assigned to Sn–N stretching vibration. Absorption at 1120 and 1489 cm^{-1} are assigned to ν(C=S) and ν(C–N). In addition, a middle intensity band at 624 cm^{-1} is attribute to ν(Sn–O–Sn) which indicates a Sn–O–Sn bridged structure. The weak bands due to ν(Sn–C) appear at 553, 610 cm^{-1}, which suggesting a non-linear *trans*-configuration of the C–Sn–C moiety [13]. The above information is consistent with the analysis of the X-ray crystallography.

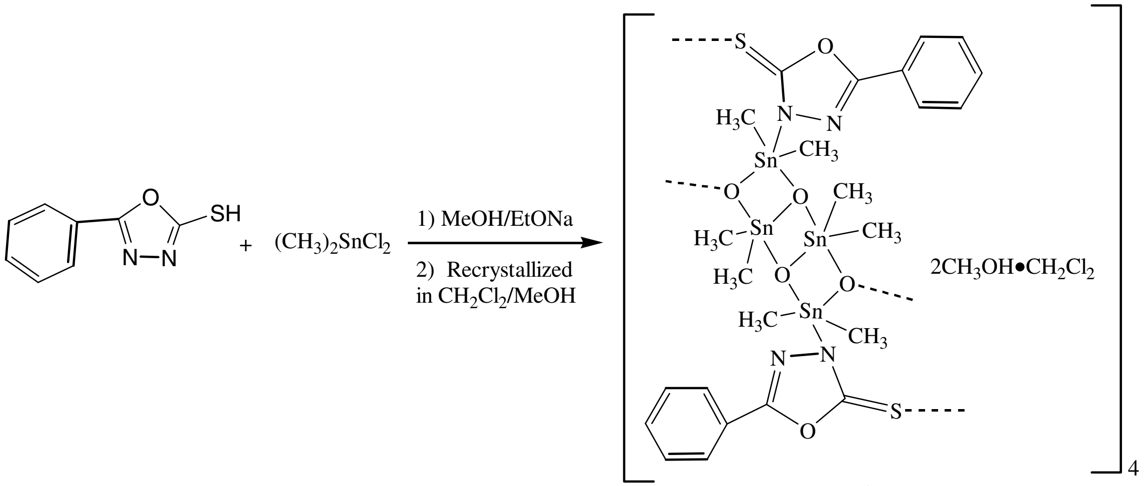
In ^{1}H NMR spectra of the free ligand, single resonance is observed at 1.63 ppm, which is absent in the spectra of the complex, indicating the tautomerism of the ligand. Complementary information for complex **1** is given by the value of the coupling constant. The $^1J_{SnC}$ value for **1** are 660 Hz, and the calculated θ (C–Sn–C) by the Holeček and Lyčka equation [14] are 132.7°, which are close to the angle 134.6(4)° observed in the solid state for complex **1**. The ^{119}Sn NMR spectrum of complex **1** showed only one type of tin atom. Holeček et al. [15] have suggested δ values from +200 to −60 for four-coordinated, −90 to −190 for five-coordinated and −210 to −400 ppm for six-coordinated tin atoms in solution. Thus the signals at −193.1 and −203.2 ppm are at the extreme end of the range for five-coordinated tin. So it can reasonably be assumed that the structure of complex **1** in solution is similar to that observed in the solid state.

2.3. Description of the crystal structure of complex 1

Further structural information was obtained by X-ray diffraction characterization in the solid state and the corresponding data are list in Table 1. The molecular structure and the macrocycle structure are shown in Figs. 1 and 2. Selected bond distances (Å) and angels (°) are listed in Table 2.

Table 1
Crystal data and structure refinement parameters for complex **1**

Empirical formula	$C_{27}H_{44}Cl_2N_4O_8S_2Sn_4$
Formula weight	1162.44
Crystal system	monoclinic
Space group	*C*2/*c*
a (Å)	15.514(10)
b (Å)	14.588(10)
c (Å)	19.542(13)
α (°)	90
β (°)	93.436(10)
γ (°)	90
V (Å^3)	4415(5)
Z	4
D_c (Mg m^{-3})	1.749
Absorption coefficient (mm^{-1})	2.495
F(000)	2256
Crystal size (mm)	0.34 × 0.18 × 0.11
θ Range (°)	1.92–25.03
Index ranges	$-8 \leqslant h \leqslant 18$; $-17 \leqslant k \leqslant 17$; $-22 \leqslant l \leqslant 23$
Reflections collected	11 359
Independent reflections [R_{int}]	3898 [0.0358]
Refinement method	full-matrix least-squares on F^2
Maximum and minimum transmission	0.7709 and 0.4842
Data/restraints/parameters	3898/11/222
Goodness-of-fit on F^2	1.059
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0361$, $wR_2 = 0.0846$
R Indices (all data)	$R_1 = 0.0629$, $wR_2 = 0.1004$
Largest difference in peak and hole (e Å^{-3})	0.808 and −0.455



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Scheme 1.