

二维网状有机锑对氨基苯乙酸酯的合成、表征及晶体结构研究

温丽媛 尹汉东* 王大奇
(聊城大学化学化工学院, 聊城 252059)

关键词: 有机锑羧酸酯; 对氨基苯乙酸; 合成; 晶体结构

中图分类号: O614.53*1 文献标识码: A 文章编号: 1001-4861(2009)08-1470-04

Synthesis, Characterization and Crystal Structure of A 2D Organoantimony Complex (C₆H₅)₃Sb(O₂CCH₂C₆H₄NH₂-*p*)₂

WEN Li-Yuan YIN Han-Dong* WANG Da-Qi
(School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059)

Abstract: The title complex bis(4-aminophenylacetate)triphenylantimony(V) has been synthesized by the reaction of triphenylantimony dibromide with 4-aminophenylacetic acid in 1:2 molar ratio. The complex was characterized by elemental analysis, IR spectra, NMR (¹H, ¹³C) and X-ray diffraction crystal structure analysis. This complex crystallizes in the monoclinic system, space group *C2/c* with *a*=2.279 4(2) nm, *b*=0.957 10(10) nm, *c*=1.335 49(15) nm, β =93.781(2)°. The molecular structure adopts a distorted trigonal bipyramidal geometry around the antimony atom. In the crystal structure molecules are connected by intermolecular N-H...O hydrogen-bonding interactions forming a two-dimensional network structure. CCDC: 726039.

Key words: organoantimony carboxylate; 4-aminophenylacetic acid; synthesis; crystal structure

Organoantimony(V) complexes have been intensively studied owing to their versatile bonding modes^[1-5] and the biological perspective^[6-10]. Therefore, synthesis of new organoantimony complexes and studies of their structures and properties are of interest in modern coordination chemistry.

In addition, carboxylates as versatile ligands were shown to act as unidentate, bidentate or bridging ligands^[11-13] in organoantimony(V) complexes by X-ray diffraction techniques. In our previous work, we have studied the coordination chemistry of this type of ligands in organoantimony complexes, the structure analyses revealed that the coordination mode of these

ligands are varied dramatically according to distinct R groups of the precursor Ph₃SbR₂^[14,15]. In order to further develop the chemistry of organoantimony carboxylates, we have synthesized the title complex. The complex have been characterized by elemental analyses, IR spectra and NMR (¹H, ¹³C) spectra. Furthermore, X-ray diffraction was also performed to determine its crystal structure.

1 Experimental section

1.1 Materials and measurements

All reagents were commercially available, and were used without further purification. Solvents were

收稿日期: 2009-04-27。收修改稿日期: 2009-06-04。

国家自然科学基金(No.20771053)和山东省自然科学基金(No.Y2008B48)资助课题。

*通讯联系人。E-mail: handongyin@lccu.edu.cn

第一作者: 温丽媛, 女, 25 岁, 硕士研究生; 研究方向: 金属有机化学。

dried and distilled before use. The elemental analyses were performed on a PE-2400-II elemental analyzer. IR spectra were recorded on a Nicolet-460 spectrophotometer as KBr discs. X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo $K\alpha$ ($\lambda=0.071\,073$ nm) radiation. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury Plus-400 NMR spectrometer and the chemical shifts were reported in ppm relative to TMS, CDCl_3 .

1.2 Preparation of the title complex

The reaction was carried out under nitrogen atmosphere. 4-Aminophenylacetic acid (0.302 g, 2 mmol) and sodium ethoxide (2.4 mmol) were added to a stirred solution of methanol (30 mL) in a Schlenk flask and stirred for 0.5 h. Triphenylantimony dibromide (0.423 g, 1 mmol) was then added to the reactor and the reaction mixture was stirred for 12 h at room temperature. The resulting clear solution was evaporated under vacuum. The product was crystallized from a mixed of dichloromethane/ether (1:1) to yield colourless blocks of crystals, yield 86%, m.p. 103~105 °C. Anal. Calcd. for $\text{C}_{34}\text{H}_{31}\text{N}_2\text{O}_4\text{Sb}$ ($M_w=653.36$)(%): C, 62.50; H, 4.78; N, 4.29. Found(%): C, 62.39; H, 4.83; N, 4.37%. IR (KBr, cm^{-1}): 3 439(m, N-H), 3 058(m, Ar-H), 1 636(s, C=O), 518(s, Sb-C), 458(s, Sb-O). ^1H NMR (400 MHz, CDCl_3 , 25 °C): 7.92 (m, 2H, Sb-PhH), 7.78 (d, $J=7.2$ Hz, 4H,

Sb-PhH), 7.26~7.44 (m, 12H, Sb-PhH and PhH), 6.80 (d, $J=8.0$ Hz, 2H, PhH), 6.62 (m, 1H, PhH), 6.53 (d, $J=8.4$ Hz, 2H, PhH), 3.29 (s, 8H, CH_2 and NH_2). ^{13}C NMR: (100 MHz, CDCl_3 , 25 °C): 175.80 (COO), 137.44, 129.36, 129.00, 128.83 (Sb-PhC), 144.74, 130.84, 130.16, 129.08, 115.30, 115.00(PhC), 42.41(CH_2).

1.3 X-ray crystal structure analyses

Single crystals suitable for X-ray structure analysis were carefully selected. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073$ nm) at 298(2) K using the U/x scan technique. A total of 7 449 reflections were collected in the range of $1.79^\circ \leq \theta \leq 25.01^\circ$ using SMART program, of which 2 562 were unique ($R_{\text{int}}=0.039\,7$) and 2 165 with $[I>2\sigma(I)]$ were considered as observed. The structures were solved by the direct method and different Fourier syntheses, and refined by full-matrix least squares on F^2 using the SHELX-97 program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions with methyl C-H distances of 0.096 nm, aromatic C-H distances of 0.093 nm and amino N-H distances of 0.086 nm and riding on carrier atoms. Crystallographic data and experimental details of the structure determinations are listed in Table 1.

CCDC: 726039.

Table 1 Crystal data and structure refinement details for the complex

Empirical formula	$\text{C}_{34}\text{H}_{31}\text{N}_2\text{O}_4\text{Sb}$	$D_c / (\text{Mg} \cdot \text{m}^{-3})$	1.493
Formula weight	653.36	$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	0.991
Temperature / K	298(2) K	$F(000)$	1 328
Wavelength / nm	0.071 073	Crystal size / mm	0.24×0.15×0.05
Crystal system	Monoclinic	θ range for data collection / (°)	1.79~25.01
Space group	$C2/c$	$h\ k\ l$ Limiting indices	-27~-21, -11~-11, -14~-15
a / nm	2.279 4(2)	Reflections collected	7 449
b / nm	0.957 10(10)	Unique reflections (R_{int})	2 562 (0.039 7)
c / nm	1.335 49(15)	Goodness-of-fit on F^2	1.028
β / (°)	93.781(2)	$R_1, wR_2 [I>2\sigma(I)]$	0.035 3, 0.069 8
V / nm^3	2.907 2(5)	R_1, wR_2 (all data)	0.047 1, 0.073 4
Z	4	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	588 and -318

2 Results and discussion

2.1 Spectral characterization

The infrared spectroscopic data provide further

support for the molecular constitution of the complex. In the IR spectra of ligands, the stretching vibration bands of O-H appear at 3 000~3 300 cm^{-1} , which disappear from the spectra of the complex. The disappea-

rance of $\nu_{\text{O-H}}$ indicating that deprotonation and subsequent coordination of the carboxylate group with antimony metal have occurred as expected. In addition, the frequencies of Sb-C deformations appear between 500 and 570 cm^{-1} , which are consistent with the literature^[16]. The formation of Sb-O bond is further supported by the appearance to a weak to medium intensity band in the region 420~460 cm^{-1} and is assigned to $\nu_{\text{Sb-O}}$ ^[17].

In the ^1H NMR spectra of the free ligands, the single resonance of the -COOH group is observed at δ 10.85 ppm and is absent in the spectra of the complex, thus indicating the deprotonation of the -COOH group and confirming that the carboxylate ligand coordinate to the antimony atom. The signals for CH_2 and NH_2 protons in the complex appeared at δ 3.29 ppm as singlet. And the aryl protons of the complex appeared at

δ 6.53~7.92 ppm as multiplet and do not allow any clear interpretation. They shift downfields 0.1~0.4 ppm as compared with free ligands, as the electron density reduced when they coordinated with Sb atom.

The ^{13}C NMR spectra of the complex show a significant downfield shift of all carbon resonances compared with the free ligand because of an electron density transfer from the ligand to the acceptor. In the complex, ^{13}C signals for CH_2 appeared at δ 42.41 ppm. The ^{13}C signals due to aryl group were assigned which appeared at δ 115.00~144.74 ppm. And the signals for carbonyl appeared at δ 175.80 ppm.

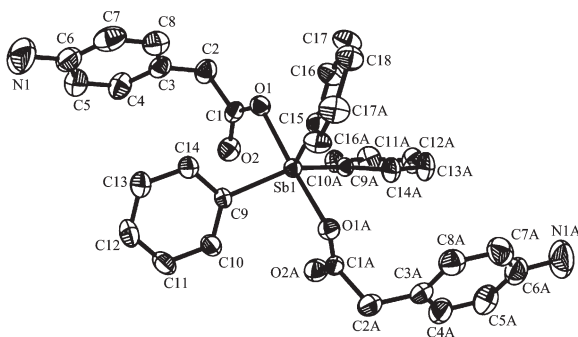
2.2 Crystal structure of the title complex

The selected bond lengths and bond angles of the complex are listed in Table 2. The molecular structure is given in Fig.1 and the packing diagram in Fig.2.

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) of the complex

Sb(1)-C(9)	0.210 2(3)	Sb(1)-C(9A)	0.210 2(3)	Sb(1)-C(15)	0.209 1(5)
Sb(1)-O(1)	0.213 5(2)	Sb(1)-O(1A)	0.213 5(2)		
C(15)-Sb(1)-C(9)	109.53(9)	C(15)-Sb(1)-C(9A)	109.53(9)	C(9)-Sb(1)-C(9A)	140.93(19)
C(15)-Sb(1)-O(1)	87.42(7)	C(9)-Sb(1)-O(1)	90.32(11)	C(9A)-Sb(1)-O(1)	91.41(11)
C(15)-Sb(1)-O(1A)	87.42(7)	C(9)-Sb(1)-O(1A)	91.41(11)	C(9A)-Sb(1)-O(1A)	90.32(11)
O(1)-Sb(1)-O(1A)	174.84(13)				

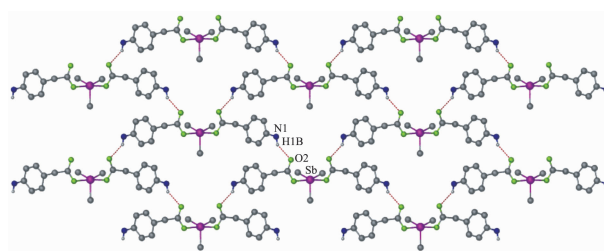
Symmetry code: (A) $-x, y, -z+3/2$.



H atoms have been omitted for clarity

Fig.1 Molecular structure of the complex, showing 50% probability displacement ellipsoids

As is shown in Fig.1, the coordination environment of the central antimony atom is five-coordinated with a slightly distorted trigonal bipyramidal geometry. Around the central Sb atom, C(9), C(9A) and C(15) occupy the equatorial plane, while O(1) and O(1A) lie in axial sites. The sum of the equatorial angles is



Symmetry code: $-x+1/2, y-1/2, -z+3/2$

Fig.2 2D network structure of the complex, for clarity, the carbon atoms which contact to the centra Sb atoms stand for the phenyl groups

359.99 $^\circ$ [C(15)-Sb(1)-C(9) 109.53(9) $^\circ$, C(15)-Sb(1)-C(9A) 109.53(9) $^\circ$, C(9)-Sb(1)-C(9A) 140.93(19) $^\circ$] and the corresponding axial-Sb-axial angle is 174.84 (13) $^\circ$, which are similar to those have found^[18] and suggest that it has slightly deviated from an ideal trigonal bipyramidal geometry. The average Sb-O bond of

0.213 5 nm is approximately equal to the sum of the covalent radii of Sb and O (0.207 nm), and lies within the range from 0.193 5 nm in triphenylstibine oxide^[19] to 0.250 6 nm in tetraphenylstibonium benzenesulphonate hydrate^[20]. The axial Sb-C in the title complex [Sb(1)-C(15) 0.209 1(5) nm, Sb(1)-C(9) 0.210 2(3) nm, Sb(1)-C(9A) 0.210 2(3) nm] are slightly shorter than the sum of the covalent radii of Sb and C (0.218 nm)^[21], which is consistent with that found in another five-coordinated trigonal bipyramidal organoantimony complex, Ph₃Sb [S₂C₂(CN)₂]^[22].

In the crystal structure, which is shown in Fig.2, molecules are connected by intermolecular N-H...O hydrogen-bonding interactions forming a two dimensional network structure. It can be seen that each discrete molecule link with other monomers through four intermolecular N(1)-H(1B)...O(2) hydrogen bonds and a 44-membered macrocycle is formed by the four such hydrogen bonds. The H(1B)...O(2), N(1)...O(2) distance and the N(1)-H(1B)...O(2) angle are 0.256, 0.329 3 nm, 143.7°, respectively. To our knowledge, this similar structure has not been reported so far.

References:

- [1] Haiduc I, Sowerby D B, Lu S F. *Polyhedron*, **1995**,**14**:3389~3472
- [2] Said M A, Kumara Swamy K C, Poojary D M, et al. *Inorg. Chem.*, **1996**,**35**:3235~3241
- [3] Breunig H J, Krüger T, Lork E. *Angew. Chem. Int. Ed. Engl.*, **1996**,**36**:615~617
- [4] Mahalakshmi H, Jain V K, Tiekink E R T. *Main Group Met. Chem.*, **2001**,**24**:391~392
- [5] Domasevitch K V, Gerasimchuk N N, Mokhir A. *Inorg. Chem.*, **2000**,**39**:1227~1237
- [6] Silvestru C, Silaghi-Dumitrescu L, Haiduc I, et al. *J. Chem. Soc. Dalton Trans.*, **1986**:1031~1034
- [7] Silvestru C, Curtui M, Haiduc I, et al. *J. Organomet. Chem.*, **1992**,**426**:49~58
- [8] Silvestru C, Haiduc I, Tiekink E, et al. *Appl. Organomet. Chem.*, **1995**,**9**:597~607
- [9] Silvestru C, Socaciu C, Baba A, et al. *Anticancer Res.*, **1990**, **10**:803~804
- [10] HU Sheng-Zhi(胡盛志), LIN Wen-Feng(林文锋). *Chinese J. Struct. Chem(Jiegou Huaxue)*, **1989**,**8**(4):249~256
- [11] Sharutin V V, Sharutina O K, Pakusina A P, et al. *J. Organomet. Chem.*, **1997**,**536**~**537**:87~92
- [12] Wieber M, Fetzter-Kremling I, Reith H, et al. *Chem. Sci.*, **1987**, **42**:815~817
- [13] Lang G, Klinkhammer K W, Recker C, et al. *Allg. Chem.*, **1998**,**624**:689~693
- [14] Wen L Y, Yin H D, Quan L, et al. *Acta Crystallogr., Sect. E*, **2008**,**64**:m1303~1303
- [15] Wen L Y, Yin H D, Wang D Q, et al. *Acta Crystallogr., Sect. E*, **2008**,**64**:m1426~1426
- [16] Gupta A, Sharma R K, Bohra R, et al. *J. Organomet. Chem.*, **2002**,**645**:118~126
- [17] Garje S S, Jain V K. *Main Group Met. Chem.*, **1995**,**18**:387~390
- [18] LIU Xiao-Lan(刘小兰), LIU Yan-Qiu(刘延秋), ZHOU Wei-Hong(周卫红), et al. *Chinese J. Inorg. Chem.(Wuji Huaxue Xuebao)*, 1997,(3):270~275
- [19] Ferguson G, Glidewell C, Kaitner B, et al. *Acta Crystallogr., Sect. C*, **1987**,**43**:824~826
- [20] Ruether R, Huber F, Preut H. *J. Organomet. Chem.*, **1985**, **295**:21~28
- [21] Gupta A, Sharma R K, Bohra R, et al. *Polyhedron*, **2002**,**21**: 2387~2392
- [22] Bhandari S, Frost C G, Hague C E, et al. *J. Chem. Soc., Dalton Trans.*, **2000**:663~669