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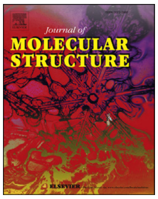

Two organoantimony (V) coordination complexes modulated by isomers of trifluoromethylbenzoate ligands: Syntheses, crystal structure, photodegradation properties

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ABSTRACT

Two organoantimony (V) coordination complexes, namely Ph_3Sb(2-tmbc) (**1**) and Ph_3Sb(3-tmbc) (**2**) (2-tmbc = 2-(trifluoromethyl)benzoic carboxyl, 3-tmbc = 3-(trifluoromethyl)benzoic carboxyl) have been synthesized and characterized by IR spectra, elemental analysis, powder X-ray diffraction (PXRD) and single-crystal X-ray diffraction. Single-crystal X-ray diffraction analysis reveals that complexes **1** and **2** show different architectures by the intermolecular hydrogen bonds (C—H···F), complex **1** displays an 1D straight chain structure, while complex **2** shows an 1D zigzag chain structure. The photodegradation properties of complexes **1** and **2** has been investigated in organic dyes (RhB, MV, MB) the results indicated that the two complexes are good candidates for the photocatalytic degradation of three dyes. The tentative photocatalytic degradations mechanism is discussed.

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1. Introduction

Over the last decades, environmental pollution caused by organic pollutants has brought more and more severe impact on human health [1]. Recently, much effort has been devoted to develop new photocatalytic materials based on metal-organic complexes (MOCs), motivated largely by a demand to solve pollution problems [2–5]. The degradation of such organic dyes is based on the generation of the hydroxyl radicals (·OH) that can rapidly oxidize a broad range of organic contaminants [6,7]. Up to now, transition metal-organic complexes are most widely studied not only for their good photocatalytic performance, chemical stability, environmentally friendly features and low production costs, but also for their diversity of structures and controllability of the synthesis [8–13]. To our knowledge, the photocatalytic performance of antimony-based MOCs has not been reported.

As one of the heavier pnictogens, antimony compounds often have coordination numbers of five by using energetically accessible 5*d* orbitals to form dsp^3 hybrid orbitals for bonding with second-period atoms such as O and N [14]. Therefore, a large number of organoantimony compounds of pentavalent states derived from carboxylates have been synthesized because of the striking structural possibilities ranging from discrete monomeric structures to supramolecular assemblies [15], and the biological application in antimicrobial properties as well as antitumor activities [16]. Although carboxylates are widely utilized in the synthesis of organoantimony carboxylates [17–25], organoantimony complexes based on H_2tmbc have rarely been investigated. The H_2tmbc not only has two carboxylate groups to bind to the metal center but also three F sites with the potential capability of participating in secondary interactions such as halogen bonds or hydrogen bonds [26], resulting in diverse supramolecular structure via coordinative and other noncovalent contacts [27].

In view of these observations, in this work, two complexes have been synthesized and characterized based on isomers of H2tmbc ligands. Their photocatalytic activities for the degradation of methylene blue (MB), rhodamine B (RhB) and methyl violet (MV) Moreover, the tentative mechanism has been discussed in this paper.

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Table 1
Summary of crystal data and structure refinement parameters for complex **1** and **2**.[a]

Parameter	1	2
Empirical formula	$C_{34}H_{23}SbF_6O_4$	$C_{34}H_{23}SbF_6O_4$
Formula weight	731.27	731.27
Crystal system	Orthorhombic	Monoclinic
space group	*Aba2*	*P2(1)/c*
a (Å)	21.4159(19)	11.1898(9)
b (Å)	15.3641(14)	16.7371(14)
c (Å)	9.4420(9)	17.0529(15)
V ($Å^3$)	3106.8(5)	3045.9(4)
F (000)	1456	1456
Crystal size (mm)	0.47 × 0.40 × 0.32	0.40 × 0.37 × 0.35
θ range for data collection (°)	2.65–25.02	2.26–25.02
Limiting indices (°)	$-25 \le h \le 24$	$-12 \le h \le 13$
	$-13 \le k \le 18$	$-19 \le k \le 11$
	$-10 \le l \le 11$	$-19 \le l \le 20$
Reflections collected/unique(R_{int})	7440/2656(0.0399)	15021/5369(0.0238)
Data/restraints/parameters	2656/1/206	5369/0/434
Goodness of fit (GOF) on F^2	1.136	1.031
Final *R* indices [I>2σ(I)]	$R1 = 0.0430$, $wR2 = 0.0986$	$R1 = 0.0290$, $wR2 = 0.0662$
R indices (all data)	$R1 = 0.0566$, $wR2 = 0.1047$	$R1 = 0.0460$, $wR2 = 0.0745$
Largest diff. peak and hole (e. $Å^{-3}$)	1.192 and −0.847	0.707 and −0.372

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR2 = [\Sigma w(Fo2 - Fc2)2]/[\Sigma w(Fo2)2]^{1/2}$.

2. Experimental

2.1. Measurement and reagents

All solvents were pretreated to get rid of the water before using. 2-(trifluoromethyl) benzoic acid, 3-(trifluoromethyl) benzoic acid, and triphenylantimony dichloride were purchased from TCI. Methylene blue, rhodamine B and methyl violet were purchased from Aladdin. The other reagents were produced in China.

Infrared spectrum were recorded as KBr pellets on the Nicolet 170SX spectrometer in the 4000-400 cm^{-1} region. Elemental analysis (C, H, and N) was performed in a model 2400 PerkinElmer analyzer. The X-ray diffraction data were collected on an Enraf-Nonius CAD-4 single crystal X-ray diffractometer. UV spectra were recorded on a Unicam UV-2 spectrometer. Powder X-ray diffraction (PXRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer with Cu-Ka (λ = 1.5418 Å) radiation at room temperature. UV–Vis diffuse reflectance spectrum (DRS) were measured from 200 to 1200 nm with a PerkinElmer Lamda 650S spectrophotometer, in which $BaSO_4$ was used as the standard with 100% reflectance.

2.2. Synthesis of complex 1 and 2

2-(trifluoromethyl) benzoic Acid or 3-(trifluoromethyl) benzoic Acid (0.424 g, 2.0 mmol) was dissolved in methanol (20 mL) and then sodium methoxide (0.108 g, 2.0 mmol) was added to the solution. The mixture was stirred at 25 °C for 2 h. Triphenylantimony dichloride (0.424 g, 1.0 mmol) was dissolved in methylbenzene (20 mL) and added to the above mixture. The resulting mixture was stirred and refluxed for 24 h, then removed solvent by evaporation under vacuum until the white solid was obtained. The solid was recrystallized in petroleum ether/dichloromethane (1:1) to give colorless crystals after 2 weeks. For the complex **1** $[Ph_3Sb(OOCC_6H_5F_3)_2]$, Elemental Anal Calc (%): C 55.84, H 3.17. Found (%): C 55.69, H 3.12. IR (KBr, cm^{-1}): 1655 (s), 1438 (s), 449 (m), 440 (m). For the complex **2** $[Ph_3Sb(OOCC_6H_5F_3)_2]$, Elemental Anal Calc (%): C 55.84, H 3.17. Found (%): C 55.95, H 3.22. IR (KBr, cm^{-1}): 1651 (s), 1436 (s), 453 (m), 449 (m).

2.3. X-ray structure determination

Single crystals with dimensions of 0.47 × 0.40 × 0.32 (**1**), 0.40 × 0.37 × 0.35 (**2**) were mounted on an Enraf-Nonius CAD-4 X-ray singlecrystal diffractometer. All data were collected at 293(2) K with graphite monochromated MoKa radiation (λ = 0.71073 Å) in ω-2θ scan mode. The structures were solved by direct methods using SHELXS-97 [28]. The non-hydrogen atoms were defined by the Fourier synthesis method. Positional and thermal parameters were refined by the full matrix least-squares method (on F^2) to convergence [29]. All structures were examined using the Addsym subroutine of PLATON [30] to ensure that no additional symmetry could be applied to the models. Crystallographic data for complexes **1** and **2** are given in Table 1. Selected bond lengths and angles for complexes **1** and **2** are listed in Table 2.

2.4. Photocatalytic activity test

The photocatalytic activities of complexes **1** and **2** were evaluated by the photodegradation of MB, RhB and MV solutions at ambient temperature (298 K). The photocatalytic reactions were performed by a typical process [31]: 25 mg of coordination complex was dispersed in 100 mL aqueous solution of MB (6 mg • L^{-1}), RhB (6 mg • L^{-1}) or MV (6 mg • L^{-1}) under UV lamp, respectively. Before

Table 2
Selected bond lengths (Å) and angles (°) for Complex **1** and **2**.

Complex 1		Complex 2	
Sb(1)-C(9)	2.112(6)	Sb(1)-C(29)	2.105(3)
Sb(1)-C(9)#1	2.112(6)	Sb(1)-C(23)	2.109(3)
Sb(1)-C(15)	2.122(9)	Sb(1)-O(1)	2.109(2)
Sb(1)-O(1)	2.124(4)	Sb(1)-C(17)	2.109(3)
Sb(1)-O(1)#1	2.124(4)	Sb(1)-O(3)	2.113(2)
C(9)-Sb(1)-C(9)#1	140.0(4)	C(29)-Sb(1)-C(23)	138.57(13)
C(9)-Sb(1)-C(15)	109.98(19)	C(29)-Sb(1)-O(1)	91.13(10)
C(9)#1-Sb(1)-C(15)	109.98(19)	C(23)-Sb(1)-O(1)	92.97(10)
C(9)-Sb(1)-O(1)	92.8(2)	C(29)-Sb(1)-C(17)	111.22(12)
C(9)#1-Sb(1)-O(1)	89.5(2)	C(23)-Sb(1)-C(17)	110.16(12)
C(15)-Sb(1)-O(1)	86.58(18)	O(1)-Sb(1)-C(17)	86.68(10)
C(9)-Sb(1)-O(1)#1	89.5(2)	C(29)-Sb(1)-O(3)	90.68(10)
C(9)#1-Sb(1)-O(1)#1	92.8(2)	C(23)-Sb(1)-O(3)	90.81(10)
C(15)-Sb(1)-O(1)#1	86.58(18)	O(1)-Sb(1)-O(3)	172.02(8)
O(1)-Sb(1)-O(1)#1	173.2(4)	C(17)-Sb(1)-O(3)	85.42(10)

Symmetry codes: complex 1: −x, −y, z.

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