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Syntheses and crystal structures of three bis(triorganotin) benzenedicarboxylates

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Abstract: Three bis(triorganotin) benzenedicarboxylates, $1,n\text{-C}_6\text{H}_4(\text{COOSnR}_3)_2$ ($n, R=3, \text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2$, **1**; $4, \text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2$, **2**; $4, \text{C}_6\text{H}_{11}\text{-c}$, **3**), were synthesized by the reaction of 1,3 or 1,4-benzenedicarboxylic acid with triorganotin chlorides in the solution of $\text{CH}_3\text{ONa-CH}_3\text{OH}$ and characterized by means of elemental analysis, Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR) (^1H , ^{13}C , and ^{119}Sn) spectra, and X-ray single-crystal diffraction. Compounds **1–3** are all di-nuclear tin complexes in which the carboxylate is monodentate and each tin atom possesses a distorted SnC_3O tetrahedral geometry.

Keywords: complex; crystal structure; organotin; organotin carboxylate.

Introduction

Organotin compounds are widely used in industrial and agricultural production such as polyvinyl chloride (PVC) stabilizers, biocides, acaricides, catalysts, and surface curing agents (Davies et al., 2008). Organotin carboxylates, a class of organotin compounds, have been attracting great attention because of their structural diversity and biological properties, particularly anti-tumor activity (Tiekink, 1994; Ma et al., 2005, 2012; Davies et al., 2008; Hadjikakou and Hadjiliadis, 2009; Amir et al., 2014). Triorganotin carboxylates usually possess discrete structures and chain or macro-cyclic structures formed by the carboxylate ligand bridging two tin centers ($\text{Sn-O-C=O} \rightarrow \text{Sn}$) (Tiekink, 1994; Chandrasekhar

et al., 2002; Davies et al., 2008). A large variety of triorganotin carboxylates from aliphatic and aromatic carboxylic acids were synthesized and structurally characterized by X-ray single diffractions (Tiekink, 1994; Chandrasekhar et al., 2002; Davies et al., 2008; Shang et al., 2011; Ma et al., 2012; Amir et al., 2014; Zhang et al., 2014). Recently, we also reported the syntheses and crystal structures of some triorganotin carboxylates (Tian et al., 2013, 2015; Dong et al., 2014; Zhang et al., 2016; Yao et al., 2017). In order to continue to expand the structural chemistry of triorganotin carboxylates and further explore the effects of alkyls bound to tin atom on the molecular structures, we select the bulky alkyltin chlorides as organotin precursor and synthesize three bis(triorganotin) benzenedicarboxylates, $1,n\text{-C}_6\text{H}_4(\text{COOSnR}_3)_2$ ($n, R=3, \text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2$, **1**; $4, \text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2$, **2**; $4, \text{C}_6\text{H}_{11}\text{-c}$, **3**), and determine their crystal structures.

Results and discussion

Synthesis

Compounds **1–3** were prepared by the reaction of 1,3- or 1,4-benzenedicarboxylic acid with triorganotin chlorides in the molar ratio 1:2 in the solution of $\text{CH}_3\text{ONa-CH}_3\text{OH}$, which can be represented by the following equation:

These compounds are all colorless crystals and are soluble in common organic solvents such as methanol, acetone, benzene, and chloroform.

Spectroscopic analysis

The infrared spectra of the complexes do not show a broad band at $\sim 3300\text{ cm}^{-1}$ assigned to $\nu(\text{O-H})$, indicating

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the deprotonation of the carboxylic acids. The appearance of a band at $\sim 490\text{ cm}^{-1}$ assignable to the Sn-O stretching vibration confirms the formation of a Sn-O bond (Xie et al., 1989; Ma et al., 2005; Zhang et al., 2014). The strong bands at $\sim 1630\text{ cm}^{-1}$ and $\sim 1330\text{ cm}^{-1}$ are assigned to the asymmetrical stretching vibration [$\nu_{\text{as}}(\text{COO})$] and symmetrical stretching vibration [$\nu_{\text{s}}(\text{COO})$] of the carboxylates, respectively. In organotin carboxylates, infrared (IR) spectroscopy can provide useful information concerning the coordination mode of the carboxylate group. Generally, the difference between the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ bands, $\Delta\nu(\text{COO})$, of the bidentate carboxylate group is smaller than 200 cm^{-1} , while the unidentate carboxylate is larger than 200 cm^{-1} (Deacon and Phillips, 1980). The magnitudes ($283\text{--}318\text{ cm}^{-1}$) of $\Delta\nu(\text{COO})$ in **1–3** indicate that the carboxylate groups are coordinated to tin atoms in a monodentate mode in the solid state, which is in agreement with the X-ray diffraction analyses of **1–3** below.

In the ^1H NMR spectra of the compounds, the proton resonances of carboxylic acids are not observed, which further confirm the replacement of the carboxylic acid protons. In **1**, the proton signals of 1,3-benzenedicarboxylate ligand appear at 7.53, 8.32, and 9.03 ppm, and in **2** and **3**, a single peak at 8.20 ppm is assigned to the proton resonances of 1,4-benzenedicarboxylate. The proton resonances of alkyl on the tin atom lie in the normal ranges.

The ^{13}C chemical shifts of the carboxyl in **1–3** appear at 173 ppm. The resonance signals of the 2-methylpropyl group carbons in **1** and **2** are in the range 32–38 ppm, and the resonances of cyclohexyl in **3** appear in the range

26–35 ppm. The spin-spin coupling constants, $J(^{119}\text{Sn}\text{--}^{13}\text{C})$, are in the range of 326–342 Hz, which are characteristic of the four-coordinate tin atoms (Nadvornik et al., 1984; Tian et al., 2015). The ^{119}Sn chemical shifts primarily depend on the coordination number and the nature of the donor atom directly bound to the central tin atom (Davies et al., 2008). The complexes **1–3** exhibit a single ^{119}Sn resonance at 105.1, 104.8, and 16.3 ppm, respectively, which fall well within the range proposed for the four-coordinate tin centers (Nadvornik et al., 1984; Holecck et al., 1986; Willem, et al., 1998). Thus, the tin atoms in the complexes have four-coordinate environments in the CDCl_3 solution.

Structure analysis

The molecular structures of **1–3** are shown in Figures 1–3. The selected bond lengths and bond angles are listed in Table 1. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ and is a di-nuclear tin complex in which each tin atom is a four coordinate and possesses a distorted SnC_3O tetrahedral geometry with the bond angles of $94.89(11)^\circ\text{--}118.64(12)^\circ$ (Figure 1). The four coordination atoms of the tin atom come from the three carbon atoms of the 2-phenyl-2-methylpropyl groups and a carboxylate oxygen atom, which is monodentate to the tin atom. The tetrahedral nature of tris(2-methyl-2-phenylpropyl)tin carboxylates arises from the crowding of the three organic groups covalently bonded to the tin atom, and such compounds are an exception to the observation that trialkyltin

Figure 1: The molecular structure of **1**.

Displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity.

Figure 2: The molecular structure of **2**.

Displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity.

Figure 3: The molecular structure of **3**.

Displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity. Unlabeled atoms are related to labeled atoms by $-x+1/2$, $-y+3/2$, $-z+1$.

carboxylates auto-associate into polymers through carboxylate bridging (Tiekink, 1994; Chandrasekhar et al., 2002). The four bond lengths to Sn (Table 1) are similar to those found in other reported tris(2-methyl-2-phenylpropyl)tin carboxylates, such as 3,5-di-*tert*-butyl-4-hydroxybenzoate (Ding et al., 2012), and 2,6-pyridinedicarboxylate (Wang et al., 2014). The $\text{Sn}(1) \cdots \text{O}(2)$ and $\text{Sn}(2) \cdots \text{O}(4)$ separations of 2.896(2) and 3.030(2) Å are not indicative of a significant interaction between these atoms. The major stereochemical roles of atoms O(2) and O(4) are to distort the tetrahedral geometry by opening up the bond angles C(2)-Sn(1)-C(3) and C(5)-Sn(2)-C(6) to 118.64(12)° and 118.63(12)°, and reducing the O(1)-Sn(1)-C(1) and

O(3)-Sn(2)-C(4) to 96.04(12)° and 94.89(11)°, respectively. The monodentate mode of coordination of the carboxylate group is also reflected in the two disparate C-O bond lengths C(7)-O(1) of 1.289(4) Å and C(7)-O(2) of 1.222(4) Å, and C(8)-O(3) of 1.297(4) Å and C(8)-O(4) of 1.216(4) Å. The carboxylate groups and phenyl ring from the 1,3-benzenedicarboxylate ligand are not in the same plane, and the dihedral angles between the phenyl ring and each of the two carboxylate planes are 9.80(1)° and 19.82(1)°, respectively, and the dihedral angle between the two carboxylate planes is 14.43(2)°.

Tetrahedral coordination of the tin atom is also observed in compound **2** (Figure 2), the two tin atoms

Table 1: Selected bond lengths (Å) and angles (°) for **1–3**.

1					
Sn(1)–O(1)	2.092(2)	Sn(2)–O(3)	2.076(2)	C(7)–O(1)	1.289(4)
Sn(1)···O(2)	2.896(2)	Sn(2)···O(4)	3.030(2)	C(7)–O(2)	1.222(4)
Sn(1)–C(1)	2.151(3)	Sn(2)–C(4)	2.147(3)	C(8)–O(3)	1.297(4)
Sn(1)–C(2)	2.141(3)	Sn(2)–C(5)	2.142(3)	C(8)–O(4)	1.216(4)
Sn(1)–C(3)	2.139(3)	Sn(2)–C(6)	2.145(3)		
O(1)–Sn(1)–C(1)	96.04(12)	C(3)–Sn(1)–C(1)	113.38(13)	C(5)–Sn(2)–C(6)	118.63(12)
O(1)–Sn(1)–C(2)	103.13(11)	C(2)–Sn(1)–C(1)	115.08(13)	O(3)–Sn(2)–C(4)	94.89(11)
O(1)–Sn(1)–C(3)	106.82(12)	O(3)–Sn(2)–C(5)	105.76(11)	C(5)–Sn(2)–C(4)	115.24(12)
C(3)–Sn(1)–C(2)	118.64(12)	O(3)–Sn(2)–C(6)	105.27(12)	C(6)–Sn(2)–C(4)	113.18(13)
2					
Sn(1)–O(1)	2.0882(17)	Sn(2)–O(3)	2.0837(18)	C(7)–O(1)	1.302(3)
Sn(1)···O(2)	2.967(2)	Sn(2)···O(4)	3.000(2)	C(7)–O(2)	1.219(3)
Sn(1)–C(1)	2.149(3)	Sn(2)–C(4)	2.155(3)	C(8)–O(3)	1.294(3)
Sn(1)–C(2)	2.147(3)	Sn(2)–C(5)	2.145(3)	C(8)–O(4)	1.216(3)
Sn(1)–C(3)	2.151(3)	Sn(2)–C(6)	2.145(3)		
O(1)–Sn(1)–C(1)	95.45(10)	C(2)–Sn(1)–C(3)	119.45(11)	C(6)–Sn(2)–C(5)	118.74(12)
O(1)–Sn(1)–C(2)	102.88(10)	C(1)–Sn(1)–C(3)	116.68(11)	O(3)–Sn(2)–C(4)	95.28(10)
O(1)–Sn(1)–C(3)	104.24(10)	O(3)–Sn(2)–C(6)	105.34(10)	C(6)–Sn(2)–C(4)	113.17(11)
C(2)–Sn(1)–C(1)	113.23(11)	O(3)–Sn(2)–C(5)	103.71(11)	C(5)–Sn(2)–C(4)	116.34(12)
3 · C₆H₆					
Sn(1)–O(1)	2.070(2)	Sn(1)–C(7)	2.162(4)	C(19)–O(1)	1.302(4)
Sn(1)···O(2)	2.899(2)	Sn(1)–C(13)	2.149(4)	C(19)–O(2)	1.211(4)
Sn(1)–C(1)	2.145(4)				
O(1)–Sn(1)–C(1)	108.29(13)	O(1)–Sn(1)–C(13)	106.29(14)	C(1)–Sn(1)–C(13)	118.95(16)
O(1)–Sn(1)–C(7)	95.49(13)	C(1)–Sn(1)–C(7)	112.32(16)	C(13)–Sn(1)–C(7)	112.54(16)

Sn(1) and Sn(2) are bridged by the two carboxylates O(1) and O(3) of the 1,4-benzenedicarboxylate ligand. The distances of Sn–O (2.0882(17) and 2.0837(18) Å) and Sn–C (2.145(3)–2.155(3) Å) are comparable to those observed in **1** (Table 1) and tris(2-methyl-2-phenylpropyl)tin 3,5-di-*tert*-butyl-4-hydroxybenzoate (Sn–O 2.074(2) Å and Sn–C 2.142(3)–2.158(3) Å) (Ding et al., 2012).

Compound **3** (Figure 3) crystallizes in a monoclinic system with the space group *C2/c*, and an asymmetric unit contains half a molecule of **3** and half a benzene molecule. The two tin atoms are equivalent (symmetry code: $-x+1/2, -y+3/2, -z+1$) due to the presence of an inversion center in the molecule, and the coordination geometry of the tin atom is a distorted tetrahedron with the bond angles of 95.49(13)°–118.95(16)°. The covalent Sn(1)–O(1) distance (2.070(2) Å) and the Sn(1)···O(2) separation (2.899(2) Å) are slightly shorter than those of **2** (2.0882(17) and 3.000(2) Å), which may arise from more crowding of the three 2-methyl-2-phenylpropyl groups compared with the cyclohexyl groups. The carboxylate group and the phenyl ring are almost in the same plane, and the dihedral angle between the phenyl ring and the carboxylate plane is only 1.36(34)°. The structural features of **3** are in agreement with those reported for tricyclohexyltin carboxylates such as tricyclohexyltin 3,5-di-*tert*-butyl-4-hydroxybenzoate

(Ding et al., 2012), ferrocenecarboxylate (Dong et al., 2014), phenoxyacetate (Zhang et al., 2015), and salicylate (Zhang et al., 2016).

In summary, three bis(triorganotin) benzenedicarboxylates **1–3** were synthesized and characterized. They are all di-nuclear tin complexes in which the benzenedicarboxylate ligand binds the two tin atoms in a monodentate coordination mode via its carboxylate groups, and each tin atom possesses a distorted SnC₃O tetrahedral geometry.

Experimental

General

Tris(2-phenyl-2-methylpropyl)tin chloride was prepared according to literature procedure (Reichle, 1966). All other chemicals were of reagent grade and were used without further purification (Sinopharm Chemical Reagent Company Limited, Shanghai, China). Carbon and hydrogen analyses were determined using a Perkin Elmer 2400 Series II elemental analyzer (Perkin Elmer, Waltham, MA, USA). IR spectra were recorded on a Nicolet 470 FT-IR spectrophotometer using KBr discs in the range 4000–400 cm^{−1} (Thermo Nicolet Corporation, Madison, WI, USA). ¹H NMR spectral data were collected using a Bruker Avance HD 500 NMR spectrometer with CDCl₃ as the solvent and tetramethylsilane as the internal standard (Bruker BioSpin, Switzerland).

The ^{119}Sn NMR spectra were recorded in CDCl_3 on a Varian Mercury Vx300 spectrometer using Me_4Sn external reference (Varian Corporation, Palo Alto, CA, USA).

Synthesis of bis(triorgano)tin benzenedicarboxylates

Bis[tris(2-phenyl-2-methylpropyl)tin] 1,3-benzenedicarboxylate (1):

The compounds 1,3-benzenedicarboxylic acid (0.166 g, 1 mmol) and sodium methanoxide (0.108 g, 2 mmol) were added to 40 mL of methanol. The mixture was stirred for 10 min, and then, tris(2-methyl-2-phenylpropyl)tin chloride (1.108 g, 2 mmol) was added to the mixture, continuing the reaction for 3 h under reflux. The solution was cool to room temperature and filtered. The filtrate was evaporated under reduced pressure by a rotary evaporator. The resulting white solid was recrystallized from methanol-chloroform (1:1, V/V) and dried in a vacuum dryer for 12 h. Yield 0.923 g (77%), m.p. 104–106°C. Anal. Found: C, 67.74; H, 6.59. Calcd for $\text{C}_{68}\text{H}_{82}\text{O}_4\text{Sn}_2$: C, 68.02; H, 6.88%. Selected IR (KBr) cm^{-1} : 1644 $[\nu(\text{COO})_{\text{as}}]$, 1326 $[\nu(\text{COO})_{\text{s}}]$, $\Delta\nu(\text{COO})=318$, 493 $[\nu(\text{Sn-O})]$. ^1H NMR (CDCl_3) δ : 1.25 (s, 36H, 12 CH_3), 1.29 (s, $J(^{119}\text{Sn}-^1\text{H})=50$ Hz, 12H, 6 CH_2), 7.13 (d, $J=7.5$ Hz, 12H, *o*-H of phenyl), 7.21 (t, $J=7.5$ Hz, 6H, *p*-H of phenyl), 7.29 (t, $J=7.5$ Hz, 12H, *m*-H of phenyl), 7.53 (t, $J=7.5$ Hz, 1H, H-5), 8.32 (dd, $J=1.5$, 7.5 Hz, 2H, H-4 + H-6), 9.03 (t, $J=1.5$ Hz, 1H, H-2) ppm. ^{13}C NMR (CDCl_3) δ : 173.27 (COOSn), 150.95 (*i*-C of phenyl), 135.44 (C-4,6), 132.66 (C-2), 130.43 (C-1,3), 128.67 (C-5), 128.52 (*m*-C of phenyl), 125.90 (*p*-C of phenyl), 125.33 (*o*-C of phenyl), 37.92 ($J(^{119}\text{Sn}-^{13}\text{C})=342$ Hz, C- α), 37.71 ($J(^{119}\text{Sn}-^{13}\text{C})=20$ Hz, C- β), 33.15 ($J(^{119}\text{Sn}-^{13}\text{C})=46$ Hz, C- γ) ppm. ^{119}Sn NMR (CDCl_3) δ : 105.1 ppm.

Bis[tris(2-phenyl-2-methylpropyl)tin] 1,4-benzenedicarboxylate (2):

Compound 2 was prepared in the same way as 1, by adding

tris(2-methyl-2-phenylpropyl)tin chloride (1.108 g, 2 mmol) to 1,4-benzenedicarboxylic acid (0.166 g, 1 mmol). The colorless crystals (m.p. 121°–122°C) were obtained in a yield of 0.984 g (82%). Anal. Found: C, 68.31; H, 6.72. Calcd for $\text{C}_{68}\text{H}_{82}\text{O}_4\text{Sn}_2$: C, 68.02; H, 6.88%. Selected IR (KBr) cm^{-1} : 1645 $[\nu(\text{COO})_{\text{as}}]$, 1332 $[\nu(\text{COO})_{\text{s}}]$, $\Delta\nu(\text{COO})=313$, 491 $[\nu(\text{Sn-O})]$. ^1H NMR (CDCl_3) δ : 1.24 (s, 36H, 12 CH_3), 1.26 (s, 12H, 6 CH_2), 7.12 (d, $J=7.5$ Hz, 12H, *o*-H in phenyl), 7.20 (t, $J=7.5$ Hz, 6H, *p*-H of phenyl), 7.28 (t, $J=7.5$ Hz, 12H, *m*-H of phenyl), 8.20 (s, 4H, Ar-H) ppm. ^{13}C NMR (CDCl_3) δ : 173.22 (COOSn), 150.64 (*i*-C of phenyl), 136.33 (C-1,4), 129.75 (C-2,3,5,6), 128.51 (*m*-C of phenyl), 126.06 (*p*-C of phenyl), 125.26 (*o*-C of phenyl), 37.99 ($J(^{119}\text{Sn}-^{13}\text{C})=338$ Hz, C- α), 37.74 ($J(^{119}\text{Sn}-^{13}\text{C})=20$ Hz, C- β), 32.88 ($J(^{119}\text{Sn}-^{13}\text{C})=45$ Hz, C- γ) ppm. ^{119}Sn NMR (CDCl_3) δ : 104.8 ppm.

Bis(tricyclohexyltin) 1,4-benzenedicarboxylate (3):

Compound 3 was prepared in the same way as 1, by adding tricyclohexyltin chloride (0.808 g, 2 mmol) to 1,4-benzenedicarboxylic acid (0.166 g, 1 mmol). The colorless crystals (m.p. 138°–139°C) were obtained in a yield of 0.657 g (73%). Anal. Found: C, 58.35; H, 7.66. Calcd for $\text{C}_{44}\text{H}_{70}\text{O}_4\text{Sn}_2$: C, 58.69; H, 7.84%. Selected IR (KBr) cm^{-1} : 1624 $[\nu(\text{COO})_{\text{as}}]$, 1341 $[\nu(\text{COO})_{\text{s}}]$, $\Delta\nu(\text{COO})=283$, 489 $[\nu(\text{Sn-O})]$. ^1H NMR (CDCl_3) δ : 2.04–1.30 (m, 66H, 6 C_6H_{11}), 8.22 (s, 4H, Ar-H) ppm. ^{13}C NMR (CDCl_3) δ : 173.62 (COOSn), 136.25 (C-1,4), 129.62 (C-2,3,5,6), 34.56 ($J(^{119}\text{Sn}-^{13}\text{C})=326$ Hz, C- α), 31.09 ($J(^{119}\text{Sn}-^{13}\text{C})=16$ Hz, C- β), 28.91 ($J(^{119}\text{Sn}-^{13}\text{C})=65$ Hz, C- γ), 26.85 (C- δ) ppm. ^{119}Sn NMR (CDCl_3) δ : 16.3 ppm.

X-ray crystallography

The colorless single crystals suitable for X-ray measurements were obtained from chloroform-methanol (1:1, V/V) for 1 and 2 and

Table 2: Crystallographic and refinement data of 1–3.

Compound	1	2	3 · C ₆ H ₆
Empirical formula	C ₆₈ H ₈₂ O ₄ Sn ₂	C ₆₈ H ₈₂ O ₄ Sn ₂	C ₅₀ H ₇₆ O ₄ Sn ₂
Formula weight	1200.72	1200.72	978.49
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	18.686(3)	18.6240(13)	30.305(4)
<i>b</i> /Å	17.953(3)	18.3702(13)	9.7751(13)
<i>c</i> /Å	19.098(3)	18.9964(13)	21.403(3)
β /°	105.439(2)	106.430(1)	128.362(1)
Volume/Å ³	6175.9(17)	6233.8(8)	4971.5(12)
<i>Z</i>	4	4	4
<i>D_c</i> /(g · cm ^{−3})	1.291	1.279	1.307
μ /mm ^{−1}	0.854	0.846	1.044
<i>F</i> (000)	2488	2488	2032
Crystal size/mm	0.26 × 0.20 × 0.05	0.20 × 0.16 × 0.10	0.56 × 0.50 × 0.44
θ range/°	1.58–26.00	1.14–26.00	1.91–26.00
Tot. reflections	47023	48496	18612
Uniq. reflections, <i>R</i> _{int}	12097, 0.0463	12246, 0.0327	4885, 0.0318
Reflections with <i>I</i> > 2 σ (<i>I</i>)	9046	10317	4036
GOF on <i>F</i> ²	1.008	1.040	1.058
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> = 0.0394, <i>wR</i> = 0.0837	<i>R</i> = 0.0374, <i>wR</i> = 0.0859	<i>R</i> = 0.0380, <i>wR</i> = 0.0944
<i>R</i> indices (all data)	<i>R</i> = 0.0609, <i>wR</i> = 0.0919	<i>R</i> = 0.0463, <i>wR</i> = 0.0902	<i>R</i> = 0.0474, <i>wR</i> = 0.1061
$\Delta\rho_{\text{min}}^a$, $\Delta\rho_{\text{max}}^b$ /(e · Å ^{−3})	−0.292, 0.558	−0.286, 0.759	−0.565, 0.901

benzene for **3** by slow evaporation at room temperature. Diffractions measurements were performed on a Bruker Smart Apex imaging-plate area detector fitted with graphite monochromatized Mo-K α radiation (0.71073 Å) using the φ and ω scan technique. The structures were solved by direct methods and refined by a full-matrix least squares procedure based on F^2 using SHELXL-97 (Sheldrick, 2008). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions. Crystal data, collection procedures, and refinement results are summarized in Table 2. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1847424-1847426.

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