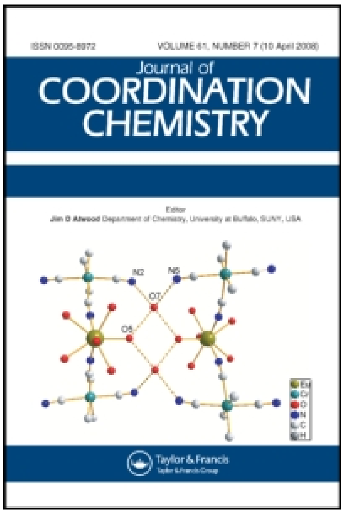

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Ladder-shaped mono-organooxotin assemblies from *n*-butylstannanoic acid and 2,4,5-trifluoro-3-methoxybenzonic acid

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A new ladder structure of $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{HF}_3\text{OCH}_3)_2\text{-}n\text{-BuSn(O}_2\text{CC}_6\text{HF}_3\text{OCH}_3)_3]_2$ (**1**) has been synthesized and characterized by elemental analysis, IR, ^{1}H, ^{13}C, ^{119}Sn NMR spectra and X-ray crystallography. All the tin atoms are six-coordinate and display distorted octahedral geometry. A series of C–H $\cdots$ F and π–π stacking interactions play an important function in the supramolecular aggregation.

Keywords: 2,4,5-Trifluoro-3-methoxybenzonic acid; Organooxotin; Assembly; C–H $\cdots$ F and π–π stacking interactions

1. Introduction

There is considerable interest in the assembly and structural analysis of organooxotin cages, clusters and coordination polymers because of their structures [1], their suitability for the construction of supramolecular frameworks [2], and their efficient catalysis of various organic reactions [3]. Several types of organooxotin clusters, such as ladder, O-capped, cube, butterfly drum, football cage and cyclic trimer have been prepared and characterized by X-ray diffraction analyses [1b, 4]. Apart from their interesting structures many organotin compounds organize into interesting supramolecular structures by a combination of covalent and non-covalent interactions. This field is quite nascent, but the recent results in this area are quite exciting. Vadapalli and co-workers reported supramolecular networks of organostannoxanes containing ferrocenyl and other substituents [5–8]. In these assemblies the supramolecular formation is assisted by a combination of non-covalent interactions including O–H $\cdots$ O, C–H $\cdots$ O, C–H $\cdots$ π and π–π stacking. Only a few examples of C–H $\cdots$ F interaction of organooxotin clusters are in the literature [8]. Our interest has focused on these studies and selected the 2,4,5-trifluoro-3-methoxybenzonic acid as ligand. Here we report the reaction of *n*-BuSn(O)OH with 2,4,5-trifluoro-3-methoxybenzonic acid, which results in a ladder structure of the type $[(n\text{-BuSn(O)O}_2\text{CC}_6\text{HF}_3\text{OCH}_3)_2\text{-}n\text{-BuSn(O}_2\text{CC}_6\text{HF}_3\text{OCH}_3)_3]_2$ (**1**).

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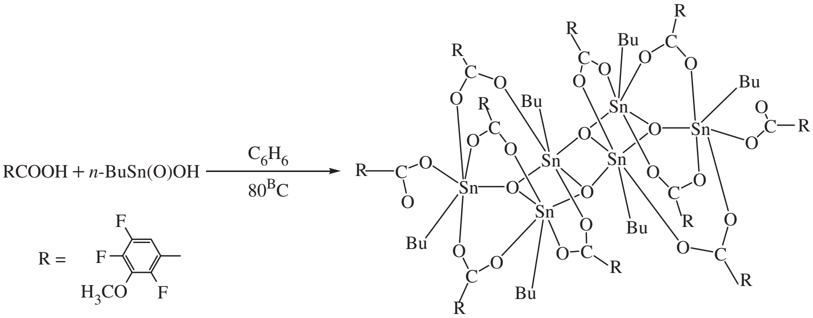

Scheme 1. Synthesis of [n-BuSn(O)$O_2CC_6HF_3OCH_3)_2$-n-BuSn($O_2CC_6HF_3OCH_3)_3]_2$.

Complex **1** has been characterized by elemental analysis, IR, ^{1}H, ^{13}C, ^{119}Sn NMR spectra and X-ray crystallography. The supramolecule was formed by a series of C–H $\cdots$ F and π–π stacking interactions.

2. Results and discussion

2.1. *Syntheses*

The synthesis is given in scheme 1.

2.2. *Spectra*

The explicit feature in the infrared spectra of **1** is the absence of the band at 2600–3436 cm^{-1}, which appears in the free ligand as the ν(O–H) vibration, indicating metal-ligand bond formation through this site. The $\Delta\nu$ value (where $\Delta\nu = \nu_{as}(COO) - \nu_s(COO)$) in the spectra of **1** (219 cm^{-1}) is comparable to those for the corresponding sodium salt. These observations suggest bidentate carboxylate [9]. The stronger absorption at 422 cm^{-1}, which is absent in the spectrum of the free ligand, is assigned to the Sn–O stretching mode. All these values are consistent with those detected in a number of organotin(IV)-oxygen derivatives [10, 14]. Another strong absorption at 694 cm^{-1} for **1** is assigned to ν(Sn–O–Sn), indicating a Sn–O–Sn bridged structure.

The ^{1}H NMR spectra show the expected integration and peak multiplicities. The resonance at 10.08 ppm in the spectrum of the free ligand is absent in the spectra of **1**, indicating loss of the carboxylic acid proton on complex formation. The ^{13}C NMR spectra of **1** show a significant downfield shift of all carbon resonances, compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor. In the ^{119}Sn NMR spectrum of **1**, three signals at -497.8, -520.2, and -598.4 ppm are assigned to the three nonequivalent tin sites in the ladder structure; the weak signal at -531 ppm is assigned to an intermediate on the way to the formation of the drum. This solution behavior is reminiscent of Holmes' observations for n-butyltin oxide carboxylate ladders [12].

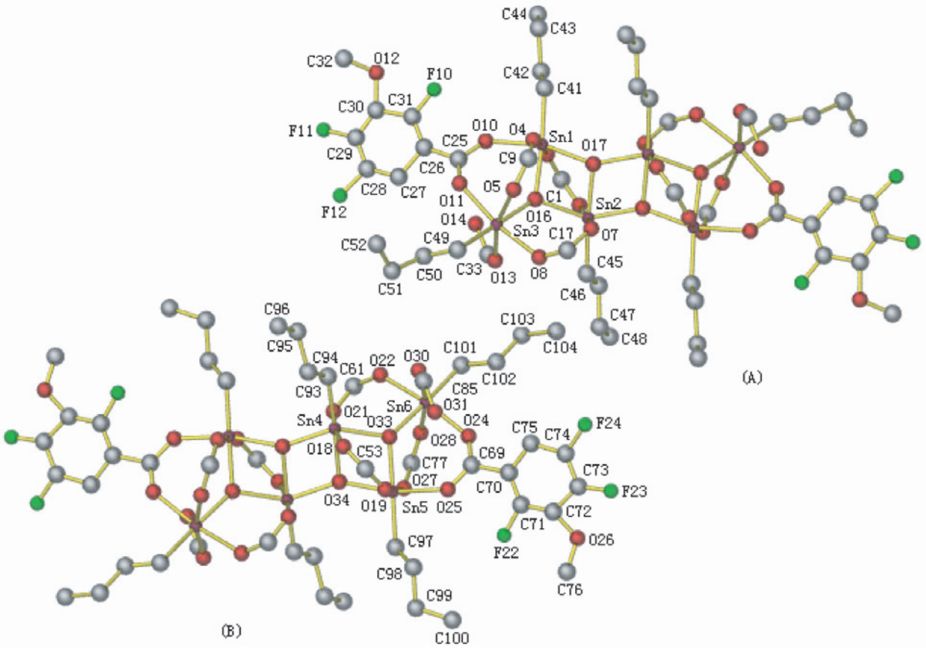

Figure 1. The molecular structure of **1**.

2.3. *Description of the crystal structure of (1)*

The molecular structure of **1** is shown in figure 1 and selected bond lengths and angles are listed in table 1. As shown in figure 1, the asymmetric unit contains two monomers (A) and (B), which are different from a crystallographic point of view. The conformations of (A) and (B) are almost the same, with only small differences in bond lengths and angles (see table 1). Each molecule of **1** has crystallographic central symmetry, which corresponds to the idealized molecular symmetry. There are, therefore, three crystallographically distinct tin atoms for each monomer. In the case of molecule (A), all the tin atoms are six-coordinate with one butyl group and five oxygen atoms, resulting in a distorted octahedral geometry. There are some differences among the three tin atoms: Sn1 is bonded to three oxygen atoms (O1, O4 and O10) from the bridging carboxylate and two μ_3-oxygen atoms (O16 and O17); Sn2 is bonded to two oxygen atoms (O2 and O7) from the bridging carboxylate in *trans* positions and three μ_3-oxygen atoms (O17, O17# and O16). The terminal Sn3 is bonded to one μ_3-oxygen atom, three oxygen atoms (O5, O8 and O11) from the bridging carboxylate and one oxygen (O13) from the perpendicular ligand. In the case of Sn3, O14 is 3.110 Å from the tin atom, indicating a very weak interaction. So Sn3 is six-coordinate, not seven-coordinate, as the literature reports [10, 12].

Examining the supramolecular structure of **1**, we find a series of intermolecular C–H$\cdots$F and π–π stacking interactions (table 2). The C–H$\cdots$F distances (2.374–2.624 Å) lie in the range 2.36–2.86 Å, which have been reported in the literature for fluorobenzenes [13]. The intermolecular π–π interactions produce a 2D plane along the *bc* plane, as shown in figure 2. The π–π distances (3.741 and 3.755 Å) are typical (3.3 to 3.8 Å) between arene planes and suggest π stacking [14–17].

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

Sn(1)–O(17)	2.064(14)	Sn(1)–O(16)	2.055(16)	Sn(4)–O(34)#2	2.064(13)
Sn(1)–C(41)	2.12(2)	Sn(1)–O(4)	2.165(16)	Sn(4)–O(34)	2.054(15)
Sn(1)–O(10)	2.160(15)	Sn(1)–O(1)	2.165(14)	Sn(4)–O(18)	2.162(13)
Sn(2)–O(17)#1	2.068(14)	Sn(2)–O(17)	2.049(15)	Sn(4)–Sn(5)	3.2227(18)
Sn(2)–C(45)	2.12(2)	Sn(2)–O(16)	2.127(15)	Sn(4)–C(93)	2.08(2)
Sn(3)–O(16)	1.989(15)	Sn(2)–O(2)	2.162(13)	Sn(4)–O(33)	2.108(14)
Sn(3)–O(11)	2.111(17)	Sn(3)–O(13)	2.049(18)	Sn(4)–O(21)	2.204(13)
Sn(3)–O(8)	2.198(16)	Sn(3)–C(49)	2.12(2)	Sn(5)–O(33)	2.032(15)
Sn(5)–C(97)	2.09(2)	Sn(3)–O(5)	2.246(17)	Sn(5)–O(34)	2.069(13)
Sn(5)–O(27)	2.179(14)	Sn(5)–O(25)	2.133(15)	Sn(5)–O(19)	2.131(14)
Sn(6)–O(30)	2.082(17)	Sn(6)–O(33)	2.016(15)	Sn(6)–C(101)	2.137(19)
Sn(6)–O(22)	2.191(14)	Sn(6)–O(24)	2.145(16)	Sn(6)–O(28)	2.230(16)
O(17)–Sn(1)–O(16)	76.2(6)	O(17)–Sn(1)–C(41)	106.8(8)	O(17)–Sn(1)–O(4)	94.1(5)
O(16)–Sn(1)–C(41)	174.9(8)	C(41)–Sn(1)–O(4)	88.1(8)	O(1)–Sn(1)–O(10)	82.4(5)
O(16)–Sn(1)–O(4)	87.6(6)	O(16)–Sn(1)–O(1)	86.7(6)	C(41)–Sn(1)–O(10)	89.5(8)
O(17)–Sn(1)–O(1)	88.1(5)	O(4)–Sn(1)–O(1)	173.2(6)	O(4)–Sn(1)–O(10)	93.8(6)
C(41)–Sn(1)–O(1)	97.5(7)	O(16)–Sn(1)–O(10)	88.1(6)	O(2)–Sn(2)–O(7)	173.6(6)
O(17)–Sn(1)–O(10)	162.1(6)	O(17)–Sn(2)–O(17)#1	74.8(6)	O(17)–Sn(2)–O(7)	90.1(6)
O(17)–Sn(2)–O(16)	75.0(6)	O(17)#1–Sn(2)–O(16)	149.8(6)	O(16)–Sn(2)–O(7)	87.5(5)
O(17)–Sn(2)–C(45)	175.6(7)	O(17)#1–Sn(2)–C(45)	101.3(8)	O(17)#1–Sn(2)–O(7)	93.0(5)
O(16)–Sn(2)–C(45)	108.8(8)	O(17)–Sn(2)–O(2)	87.6(5)	C(45)–Sn(2)–O(7)	92.2(7)
O(17)#1–Sn(2)–O(2)	92.2(5)	O(16)–Sn(2)–O(2)	86.1(5)	O(16)–Sn(3)–O(11)	90.0(6)
C(45)–Sn(2)–O(2)	90.4(7)	O(16)–Sn(3)–O(13)	87.6(7)	O(16)–Sn(3)–O(5)	85.1(6)
O(16)–Sn(3)–C(49)	174.4(8)	O(13)–Sn(3)–O(11)	105.1(7)	O(11)–Sn(3)–O(5)	87.9(6)
O(11)–Sn(3)–C(49)	90.1(9)	O(13)–Sn(3)–C(49)	97.8(9)	C(49)–Sn(3)–O(5)	89.3(8)
O(13)–Sn(3)–O(8)	87.2(7)	O(16)–Sn(3)–O(8)	87.2(6)	O(8)–Sn(3)–O(5)	79.5(6)
C(49)–Sn(3)–O(8)	91.5(8)	O(11)–Sn(3)–O(8)	167.3(6)	O(34)#2–Sn(4)–C(93)	101.6(8)
O(13)–Sn(3)–O(5)	165.1(6)	O(34)#2–Sn(4)–O(34)	75.1(6)	C(93)–Sn(4)–O(21)	91.3(7)
C(93)–Sn(4)–O(34)	175.8(7)	O(34)#2–Sn(4)–O(33)	149.6(6)	O(33)–Sn(4)–O(21)	86.5(5)
C(93)–Sn(4)–O(33)	108.8(8)	O(34)–Sn(4)–O(33)	74.6(6)	O(34)–Sn(4)–O(21)	91.4(5)
O(34)#2–Sn(4)–O(18)	93.8(5)	C(93)–Sn(4)–O(18)	90.9(7)	O(18)–Sn(4)–O(21)	172.7(5)
O(34)–Sn(4)–O(18)	86.8(5)	O(33)–Sn(4)–O(18)	86.2(5)	O(33)–Sn(5)–O(27)	88.0(6)
O(34)#2–Sn(4)–O(21)	92.5(5)	O(33)–Sn(5)–C(97)	177.6(7)	C(97)–Sn(5)–O(27)	89.8(7)
O(33)–Sn(5)–O(34)	75.9(6)	O(33)–Sn(5)–O(19)	86.1(6)	O(25)–Sn(5)–O(27)	92.4(5)
O(34)–Sn(5)–C(97)	103.5(7)	C(97)–Sn(5)–O(19)	96.2(7)	O(34)–Sn(5)–O(27)	92.8(5)
O(34)–Sn(5)–O(19)	89.7(5)	O(34)–Sn(5)–O(25)	164.9(6)	O(19)–Sn(5)–O(27)	172.8(6)
O(33)–Sn(5)–O(25)	90.1(6)	O(19)–Sn(5)–O(25)	83.6(6)	O(33)–Sn(6)–O(30)	89.7(6)
C(97)–Sn(5)–O(25)	90.8(8)	O(30)–Sn(6)–O(24)	103.5(6)	O(24)–Sn(6)–O(28)	88.0(6)
O(33)–Sn(6)–O(24)	90.9(6)	O(30)–Sn(6)–C(101)	94.4(8)	O(22)–Sn(6)–O(28)	79.4(6)
O(33)–Sn(6)–C(101)	173.7(6)	O(33)–Sn(6)–O(22)	86.5(5)	O(30)–Sn(6)–O(28)	166.9(6)
O(24)–Sn(6)–C(101)	92.8(8)	O(24)–Sn(6)–O(22)	167.3(6)	C(101)–Sn(6)–O(28)	91.2(8)
O(30)–Sn(6)–O(22)	88.9(6)	C(101)–Sn(6)–O(22)	88.8(7)	O(33)–Sn(6)–O(28)	83.9(6)

#1: $-x+1$, $-y+1$, $-z$; #2: $-x$, $-y+2$, $-z+1$.

3. Experimental details

3.1. *Materials and measurements*

2,4,5-Trifluoro-3-methoxybenzonic acid and *n*-butylstannanoic acid are commercially available and used without further purification. The melting points were obtained on a Kofler micro-melting point apparatus and are uncorrected. Infrared-spectra were recorded on a Nicolet–5700 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified. The chemical shifts were reported in ppm with respect to the references and were stated relative to external

Table 2. C–H···F and π–π interaction for **1**.

Interaction	H···F		C···F	C–H···F
C18–H18C↑F3	2.407		3.343	164.27
C101–H10E↑F9	2.599		3.442	145.57
C59–H59↑F11	2.374		3.218	150.83
C76–H76A↑F13	2.624		3.566	167.48
C32–H32A↑F15	2.461		3.265	141.05
C60–H60C↑F18	2.486		3.441	173.30
C40–H40C↑F28	2.593		3.514	161.06
C52–H52A↑F29	2.579		3.250	127.12
π(i)↑π(j)[a]	Dihedral angle (i, j) (°)	Centroid separation Cg↑Cg[b] (Å)	Cg(i)↑perp[c] (Å)	Cg(i)↑perp[d] (Å)
Cg(1)↑Cg(2)[i]	6.7	3.741	3.7210	3.6590
Cg(3)↑Cg(4)[ii]	1.6	3.755	3.4590	3.4186

[a] Cg(1), Cg(2), Cg(3) and Cg(4) refer to the centroids of C(34)–C(35)–C(36)–C(37)–C(38)–C(39), C(86)–C(87)–C(88)–C(89)–C(90)–C(91), C(10)–C(11)–C(12)–C(13)–C(14)–C(15), C(78a)–C(79a)–C(80a)–C(81a)–C(82a)–C(83a).
[b] Cg↑Cg is the distance between ring centroids; symmetry transformation: (i) x, y, z; (ii) $1+x$, $y-1$, z.
[c] Cg(i)↑perp is the perpendicular distance of Cg(i) on ring j.
[d] Cg(i)↑perp is the perpendicular distance of Cg(j) on ring i.

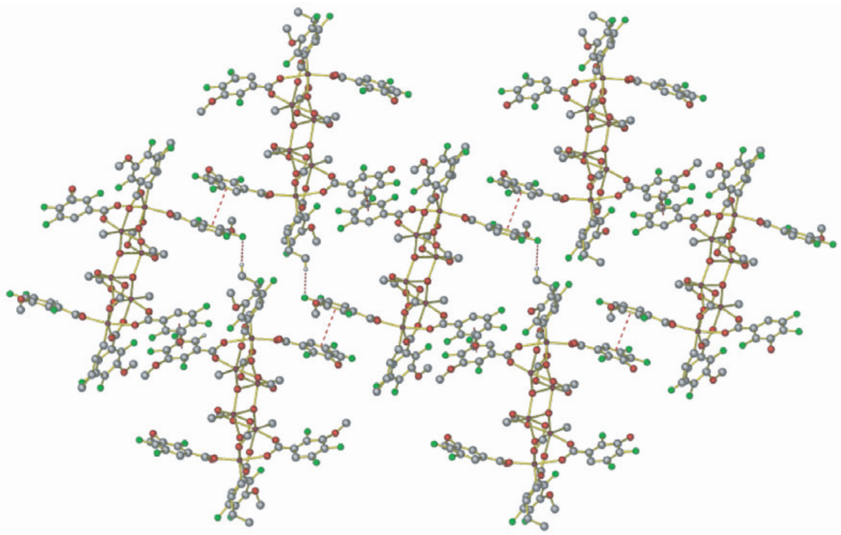

Figure 2. The 2D plane connected by intermolecular π–π interaction. Non-connected hydrogen atoms, phenyl and three carbon atoms of the butyl have been omitted for clarity.

tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400 II elemental apparatus.

3.2. *Synthesis of (1)*

All reactions were carried out under nitrogen using standard Schlenk technique. *n*-Butylstannanoic acid (0.210 g, 1 mmol) was added to the solution of 2,4,5-trifluoro-3-methoxybenzonic acid (0.412 g, 2 mmol) and the mixture was stirred under refluxing for 12 h. After filtration the solvent was evaporated *in vacuo* giving a white solid, which was recrystallized from hexane giving colorless crystals. m.p: 102–104°C Yield: 66%.

Table 3. Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_{104}H_{94}F_{30}O_{34}Sn_6$
Formula weight	3169.93
Wavelength	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	16.014(2)
b (Å)	18.255(2)
c (Å)	21.566(3)
α (°)	71.952(2)
β (°)	86.432(3)
γ (°)	87.136(3)
Z	2
Calculated density ($mg\,m^{-3}$)	1.761
$F(000)$	3120
Crystal size (mm)	$0.16 \times 0.14 \times 0.09$
θ Range (°)	1.70 to 25.01
Limiting indices	$-11 \le h \le 19$, $-21 \le k \le 19$, $-25 \le l \le 23$
Reflections collected	31,240
Unique reflection (R_{int})	20682 [$R_{int} = 0.0880$]
Refinement method	Full-matrix-block least-squares on F^2
Goodness-of-fit on F^2	0.941
Final R indices [$I > 2$ sigma(I)]	$R_1 = 0.0951$, $wR_2 = 0.2266$
R indices (all data)	$R_1 = 0.2456$, $wR_2 = 0.3040$

Anal. Calc. for $C_{104}H_{94}F_{30}O_{34}Sn_6$: C, 39.40; H, 2.99%. Found: C, 39.76; H, 3.28%. IR (KBr, cm^{-1}): ν_{as}(COO) 1618, ν_s(COO) 1399, ν(Sn–O–Sn) 694, ν_{as}(Sn–C) 584, ν_s(Sn–C) 542, ν(Sn–O) 422. ^{1}H NMR ($CDCl_3$, ppm): δ 7.32–7.65 (m, Sn–$C_6HF_3OCH_3$), δ 0.88–1.81 (m, 12H, Sn–C_4H_9), δ 4.06 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 168 (COO), 113.1, 145.3, 146.2, 148.7, 149.2, 151.1 (Ar–C), 62.5 (OCH_3), 22.8, 31.7, 45.3 (–CH_2–), 14.3 (CH_3) ppm. ^{119}Sn NMR ($CDCl_3$, ppm): −497.8, −520.2, −598.4 ppm, one additional of weak intensity appeared at −531.4 ppm.

4. X-ray crystallography studies

Crystal was mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart-1000 CCD area-detector with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXLS-97 and refined against F^2 by full matrix least squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations **1** are listed in table 3.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article (**1**) have been deposited with the Cambridge Crystallographic Data Centre as

Supplementary Publication No. CCDC: 630552 for **1**. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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