

Syntheses and characterization of triorganotin complexes: X-ray crystallographic study of triorganotin pyridinedicarboxylates with trinuclear, 1D polymeric chain and 2D network structures

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Abstract

A series of new triorganotin(IV) pyridinedicarboxylates $[(C_2H_5)_3NH][(Me_3Sn)_3(2,6-pdc)_2(H_2O)_2]$ (**1**), $[(C_2H_5)_3NH][(Ph_3Sn)_3(2,6-pdc)_2(H_2O)_2]$ (**2**), $[(C_2H_5)_3NH][{(PhCH_2)_3Sn}_3(2,6-pdc)_2(H_2O)_2]$ (**3**), $[Me_3Sn(3,5-pdc)]_n$ (**4**), $[Ph_3Sn(3,5-pdc)]_n$ (**5**), $[(PhCH_2)_3Sn(3,5-pdc)]_n$ (**6**), $[Me_3Sn_2(2,5-pdc)]_n$ (**7**), $[(Ph_3Sn)_2(2,5-pdc)]_n$ (**8**) and $[{(PhCH_2)_3Sn}_2(2,5-pdc)]_n$ (**9**) were synthesized by the reaction of trimethyltin(IV), triphenyltin(IV) or tribenzyltin(IV) chloride with 2,6(3,5 or 2,5)-H₂pdc (pdc = pyridinedicarboxylate) when triethylamine was added. Complexes **1–9** have been characterized by elemental, IR, ¹H, ¹³C and ¹¹⁹Sn NMR analyses. Among them complexes **1**, **5** and **7** have also been characterized by X-ray crystallographic diffraction analyses. Complex **1** has a trinuclear structure and forms a 2D supramolecular structure due to the coordinated water molecules via hydrogen bonds to the pendant O atoms of the carboxyl groups and the N atoms derived of the pyridine ring. Complex **5** forms a 1D polymeric chain by the intermolecular Sn ··· N (N atom derived of pyridine ring) interactions. Complex **7** has a network structure where 2,5-pyridinedicarboxylate acts as a tetradentate ligand coordinated to trimethyltin(IV) ions.

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Keywords: Pyridinedicarboxylic acid; Triorganotin; Hydrogen bond; X-ray crystallography; Supramolecular structure

1. Introduction

Organotin(IV) carboxylates have attracted much attention owing to their potential biocidal activities [1–4] and cytotoxicities [5] as well as their industrial and agricultural applications [6–11]. Among them, the study of the structural chemistry of triorganotin carboxylates has received considerable attention owing to the various structural types that may be adopted in the solid state [12–19]. Although a large number of structural studies have been carried out on the triorganostannyl esters of monofunctional carboxylic

acids [20], relatively little work has so far been undertaken on the triorganotin esters of dicarboxylic acids [21–24]. The organotin(IV) dicarboxylates have been studied in considerable detail, and in general the reported organotin(IV) dicarboxylates exist as dinuclear [25] one-dimensional zig-zag chain [26] and cyclic structures [27]. Recently, our interest has focused on triorganotin(IV) complexes containing dicarboxylate ligands which have an additional hetero-donor atom (e.g., N, O, S) residing on the R' group that is, potentially pentadentate ligands, in order to examine what effect the presence of the heteroatom has on the structure adopted by these complexes [28]. As a part of our continuing program in this area, we have synthesized and structurally characterized triorganotin(IV) pyridinedicarboxylates of 2,6(3,5 or 2,5)-pyridinedicarboxylic acid and the results of this study are reported herein.

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2. Results and discussion

2.1. Syntheses

The triorganotin(IV) pyridinedicarboxylates $[(C_2H_5)_3NH][(Me_3Sn)_3(2,6-pdc)_2(H_2O)_2]$ (**1**), $[(C_2H_5)_3NH][(Ph_3Sn)_3(2,6-pdc)_2(H_2O)_2]$ (**2**), $[(C_2H_5)_3NH]\{[(PhCH_2)_3Sn]_3(2,6-pdc)_2(H_2O)_2\}$ (**3**), $[Me_3Sn(3,5-pdc)]_n$ (**4**), $[Ph_3Sn(3,5-pdc)]_n$ (**5**), $[(PhCH_2)_3Sn(3,5-pdc)]_n$ (**6**), $[(Me_3Sn)_2(2,5-pdc)]_n$ (**7**), $[(Ph_3Sn)_2(2,5-pdc)]_n$ (**8**) and $\{[(PhCH_2)_3Sn]_2(2,5-pdc)\}_n$ (**9**) were synthesized by the reaction of trimethyltin(IV), triphenyltin(IV) or tribenzyltin(IV) chloride with 2,6-(3,5 or 2,5)-pyridinedicarboxylic acid with the mole ratio of 1:2 when triethylamine was added. The syntheses procedure is shown in Scheme 1.

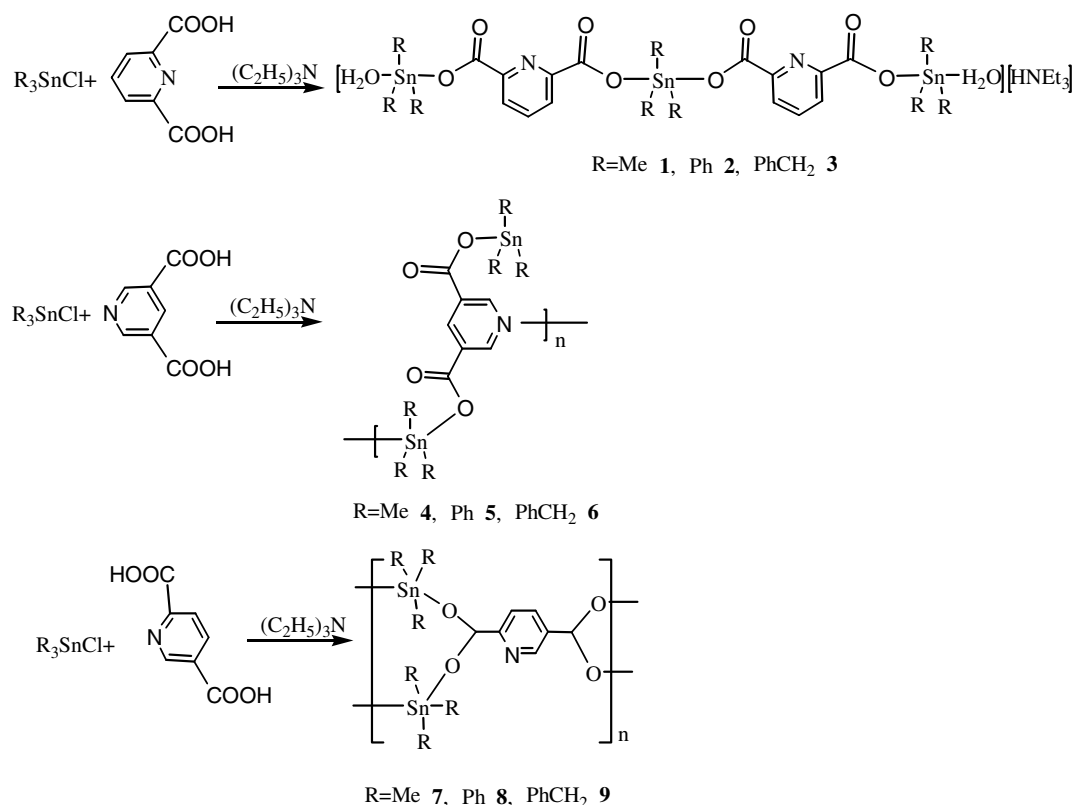
2.2. IR spectra

The infrared spectrum of the three free ligands show $\nu(C=O)$ of COOH at 1667, 1681 and 1678 cm^{-1} , respectively, as a strong band, which indicate that there are intermolecular hydrogen bonds of the type $C=O \cdots H-O$ in the uncoordinated 2,6-pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid and 2,5-pyridinedicarboxylic acid molecules. This is commonly observed in the case of carboxylic acids [29]. After deprotonation and coordinated to tin atoms, these bands disappear and are replaced by strong bands in the 1617–1623 and 1305–1433 cm^{-1} regions,

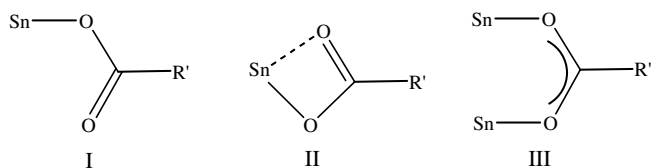
which correspond to the asymmetric and symmetric vibrations, respectively, of the COO moiety. Also strong absorption appear at 478–489 cm^{-1} in the respective spectra of the complexes **1–9**, which is absent in the spectra of the free ligand, and is assigned to the Sn–O stretching mode of vibration. All these values are consistent with that detected in a number of organotin(IV) derivatives [30–32]. The peak at about 3325 cm^{-1} in the infrared spectrum indicates the existence of the coordinated water molecules in complexes **1–3**. Besides, as reported in the literature [33,34], the IR spectra can provide useful information concerning the mode of coordination of the carboxylate in organotin complexes (coordination mode see Scheme 2). The $\Delta\nu[\nu_{as}(COO^-) - \nu_{sym}(COO^-)]$ values for complexes **1–6** (301–320 cm^{-1}) and **7–9** (184–186 cm^{-1}) reveal that the coordination mode of the carboxylate groups in **1–6** and **7–9** are mode I and III type, respectively.

2.3. NMR spectra

The 1H NMR spectra show the expected integration and peak multiplicities. The single resonance of –OH in the spectra of the free ligands are absent in the spectra of all the complexes **1–9** indicating the replacement of the carboxylic acid protons by a triorganotin moiety on complex formation. In addition, the resonances appear at 8.95–8.98 ppm for **1–3** are attributed to the protons of coordinated water molecules in the structures. The resonances



Scheme 1.



Scheme 2. Different coordination modes of the carboxylate group.

appear at 1.35–1.37 and 3.15–3.17 ppm in complexes **1–3** are owing to N-CH₂CH₃ groups.

The ¹³C NMR spectra of all complexes show a significant downfield shift of all carbon resonance compared with the free ligands. The shift is a consequence of an electron density transfer from the ligand to the acceptor. The single resonances at 170.7–173.8 are attributed to the COO groups in complexes **1–9**. These data are consistent with the structures of **1–9**.

The ¹¹⁹Sn NMR spectra of complexes **1–9** show resonances between –85 and –122 ppm. As reported in the literature [35], values of δ (¹¹⁹Sn) in the ranges –210 to –400, –90 to –190 and 200 to –60 ppm have been associated with six-, five- and four-coordinate tin centers, respectively. On this basis we can conclude that complexes **1–3** ($\delta = -112, -122$ and -118 ppm, respectively) and **7–9** ($\delta = -115, -118$ and -117 ppm, respectively) are typical of five-coordinated and **4–6** ($\delta = -85, -87$ and -88 ppm, respectively) lie between four- and five-coordinated. This is confirmed by the X-ray crystal structures of complexes **1, 5** and **7** (see Table 1).

2.4. Description of crystal structures

2.4.1. [(C₂H₅)₃NH][Me₃Sn(2,6-pdc)] (1)

The crystal structure and the unit cell of **1** are illustrated in Figs. 1 and 2, respectively. Selected bond lengths and angles are shown in Table 2.

The X-ray diffraction investigation of complex **1** shows that it is not a infinite polymeric chain but an oligomer with three trimethyltin centers linked by two 2,6-pdc ligands and bounded by two water molecules coordinating the terminal tin atoms. In the case of **1**, both the trinuclear oligomeric anion and the counter cation are subject to crystallographically imposed twofold axial symmetry. Thus Sn(2) and C(11) of the anion and N(2) and C(16) of the cation are in special positions on a twofold axis, while all other atoms of the asymmetric unit, including the methylene group involving C(15) which is disordered over two symmetry related sites of equal occupancy, are in general positions. In **1**, each dianion bridges two Sn centers via only one O atom derived from the monodentate carboxylate moiety. Owing to the coordinated water molecules, the environments of the two terminal Sn atoms are different to another Sn atom. As a result of the bidentate mode of coordination of the dicarboxylic acid, each Sn center is five-coordinate and exists in trigonal bipyramidal geometry with the O (derived of water and carboxyl groups, respectively) atoms occupying the axial sites [Sn(2)–O(3) 2.266(4), Sn(2)–O(3^{^1}) (symmetry code: $-x + 3/2, -y + 5/2, z$) 2.266(4), Sn(1)–O(1) 2.179(3), Sn(1)–O(5) 2.396(4) Å and O(3)–Sn(2)–O(3^{^1}) 165.9(2)°, O(1)–Sn(1)–O(5) 177.38(14)°].

Table 1
Crystal, data collection and structure refinement parameters for complexes **1, 5** and **7**

Complex	1	5	7
Empirical formula	C ₂₉ H ₅₃ N ₃ O ₁₀ Sn ₃	C ₄₃ H ₃₃ NO ₄ Sn ₂	C ₁₃ H ₂₁ NO ₄ Sn ₂
Formula weight	959.87	865.08	492.69
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pccn</i>	<i>P2₁/c</i>	<i>C2/c</i>
<i>a</i> (Å)	21.082(15)	10.5946(16)	13.429(9)
<i>b</i> (Å)	11.651(8)	26.490(4)	10.234(7)
<i>c</i> (Å)	16.188(11)	13.620(2)	13.604(9)
α (°)	90	90	90
β (°)	90	102.502(2)	100.226(9)
γ (°)	90	90	90
<i>Z</i>	4	4	4
<i>D</i> _{calc} (Mg m ⁻³)	1.598	1.540	1.779
<i>F</i> (0 0 0)	1900	1720	952
μ (mm ⁻¹)	1.919	1.381	2.725
Crystal size (mm)	0.52 × 0.39 × 0.24	0.49 × 0.41 × 0.26	0.58 × 0.49 × 0.43
θ Range (°)	1.93–25.02	2.11–25.03	2.52–25.01
Index ranges	–25 ≤ <i>h</i> ≤ 23; –13 ≤ <i>k</i> ≤ 12; –18 ≤ <i>l</i> ≤ 19	–12 ≤ <i>h</i> ≤ 12; –31 ≤ <i>k</i> ≤ 18; –16 ≤ <i>l</i> ≤ 15	–15 ≤ <i>h</i> ≤ 15; –12 ≤ <i>k</i> ≤ 11; –16 ≤ <i>l</i> ≤ 7
Reflections collected	19,526	19,388	4457
Unique reflections (<i>R</i> _{int})	3489 (0.0394)	6594 (0.0284)	1615 (0.0422)
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3489/73/210	6594/0/451	1615/60/91
Goodness-of-fit on <i>F</i> ²	1.005	1.003	1.001
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0309, <i>wR</i> ₂ = 0.0748	<i>R</i> ₁ = 0.0283, <i>wR</i> ₂ = 0.0610	<i>R</i> ₁ = 0.0471, <i>wR</i> ₂ = 0.1307
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0533, <i>wR</i> ₂ = 0.0856	<i>R</i> ₁ = 0.0453, <i>wR</i> ₂ = 0.0701	<i>R</i> ₁ = 0.0661, <i>wR</i> ₂ = 0.1475

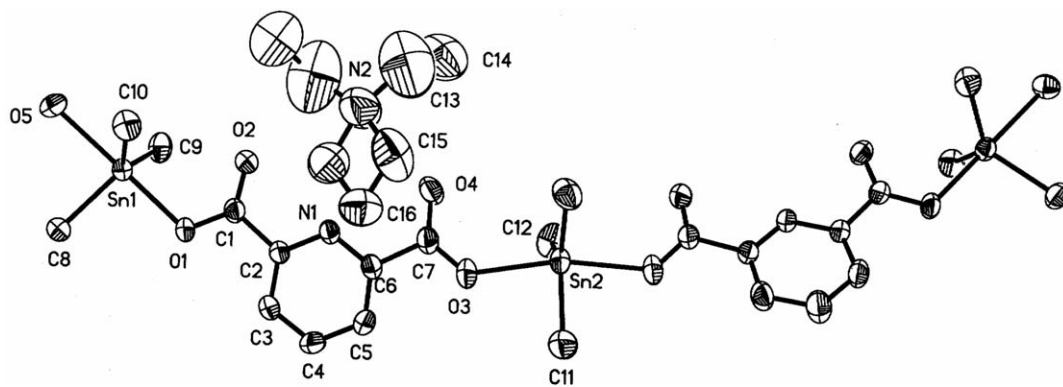


Fig. 1. Molecular structure of complex 1.

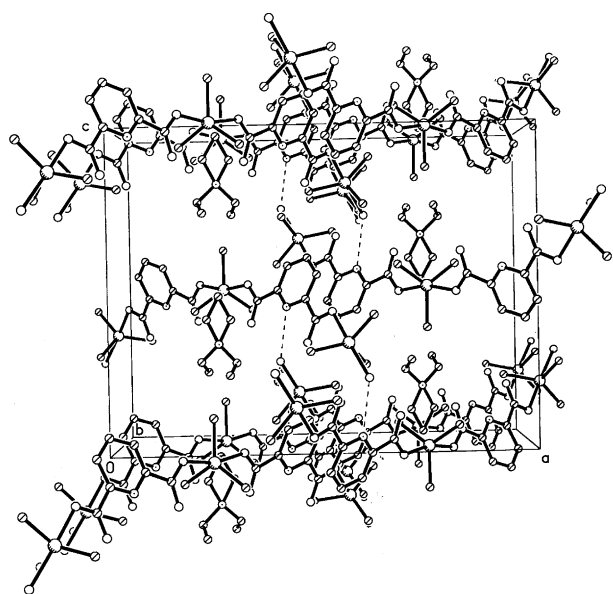


Fig. 2. The unit cell of complex 1.

Despite the rather high estimated standard deviations in the C–O bond distances a clear trend in these parameters may be discerned. As expected the C–O bond distances [C(1)–O(2) 1.225(6) Å, C(7)–O(4) 1.217(7) Å] associated with the non-coordinating O atoms are significantly shorter

than the coordinating C–O bond distances [C(1)–O(1) 1.278(6) Å, C(7)–O(3) 1.252(6) Å]. The intramolecular Sn(2)···O(4) of 3.542 Å, is not indicative of bonding interactions between these atoms. Although not involved in coordination to tin, the O(4) atom form significant intermolecular contacts in the crystal lattice.

Through the coordinated water molecule to the terminal tin atoms of the polymer, the polymers are associated with each other via hydrogen bonds to the pendant O atoms of carboxyl groups and the N atoms derived of the pyridine ring, so that a 2D network is formed and this is shown in Fig. 3. The distances of hydrogen-bonding, O(5)–H···O(2^{1^}), O(5)–H···O(4^{1^}) and O(5)–H···N(1^{1^}), separations are 2.759, 2.792 and 2.876 Å, respectively. This confirms that the water molecules play an important role in the stabilization of the polymer.

2.4.2. $[Ph_3Sn(3,5-pdc)]_n$ (5)

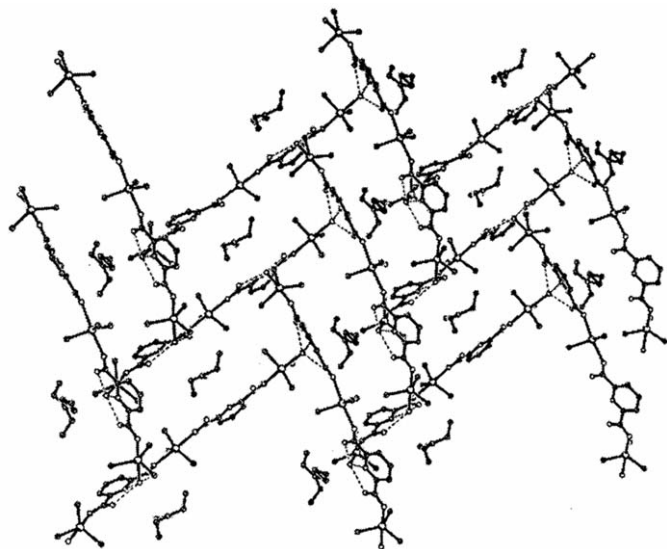
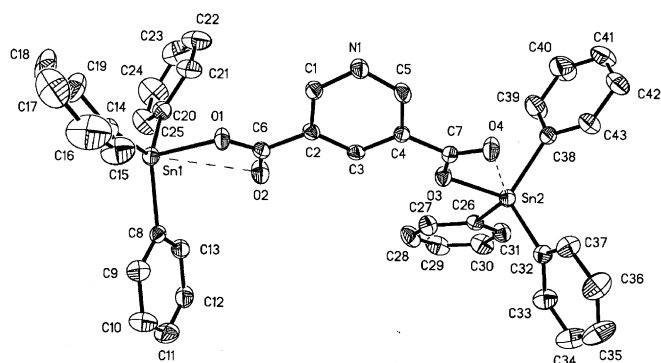
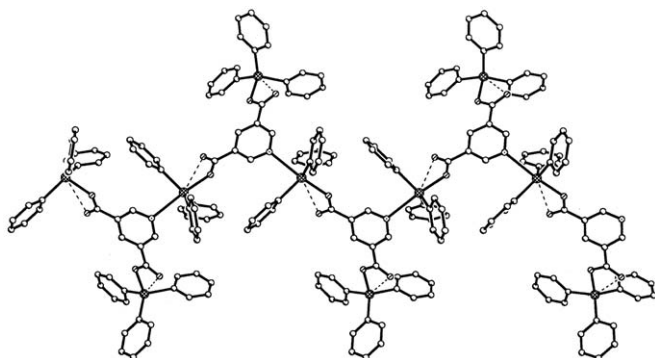
The crystal and the polymeric chain structures of 5 are illustrated in Figs. 4 and 5, respectively, selected bond lengths and bond angles in Table 2.

As can be seen from Fig. 4, complex 5 is a triphenyltin ester of 3,5-pyridinedicarboxylic acid possesses an unequivocally structure. Each 3,5-pyridinedicarboxylate dianion bridges two tin centers via only one O atom derived of the monodentate carboxylate moiety. We can see from

Table 2
Selected bond lengths (Å) and angles (°) for complex 1

Bond lengths		Bond angles			
Sn(1)–C(9)	2.105(5)	C(9)–Sn(1)–C(8)	117.7(3)	C(7)–O(3)–Sn(2)	130.3(4)
Sn(1)–C(8)	2.108(5)	C(9)–Sn(1)–C(10)	125.7(2)	O(2)–C(1)–O(1)	124.6(5)
Sn(1)–C(10)	2.116(6)	C(8)–Sn(1)–C(10)	115.3(3)	O(2)–C(1)–C(2)	120.0(5)
Sn(1)–O(1)	2.179(3)	C(9)–Sn(1)–O(1)	94.5(2)	O(4)–C(7)–O(3)	126.5(5)
Sn(1)–O(5)	2.396(4)	C(8)–Sn(1)–O(1)	92.34(19)	O(3)–C(7)–C(6)	118.8(5)
Sn(2)–C(12 ^{1^})	2.099(5)	C(10)–Sn(1)–O(1)	94.6(2)	C(11)–Sn(2)–O(3)	82.93(10)
Sn(2)–C(11)	2.090(10)	C(9)–Sn(1)–O(5)	83.5(2)	C(12)–Sn(2)–O(3 ^{1^})	97.1(2)
Sn(2)–O(3)	2.266(4)	C(8)–Sn(1)–O(5)	87.17(19)	C(11)–Sn(2)–O(3 ^{1^})	82.93(10)
C(1)–O(1)	1.278(6)	C(10)–Sn(1)–O(5)	88.0(2)	C(12)–Sn(2)–O(3)	90.4(2)
C(1)–O(2)	1.225(5)	O(1)–Sn(1)–O(5)	177.38(14)	O(3 ^{1^})–Sn(2)–O(3)	165.9(2)
C(7)–O(3)	1.252(6)	C(12)–Sn(2)–C(12 ^{1^})	116.2(4)	C(1)–O(1)–Sn(1)	115.1(3)
C(7)–O(4)	1.217(7)	C(12)–Sn(2)–C(11)	121.9(2)		

Symmetry code: ^{1^} $-x + 3/2, -y + 5/2, z$.

Fig. 3. Perspective view showing the 2D network of **1**.Fig. 4. Molecular structure of **5**.Fig. 5. The polymeric chain formed by the Sn...N intermolecular interactions of **5**.

the structure, one tin center is four-coordinated and the other is five-coordinated due to the coordinated N atom derived of the adjacent ligand. For the four-coordinated central tin atom forms four primary bonds: three to the phenyl groups and one to the oxygen atom derived of the monodentate carboxyl group. Thus, the geometry of the tin center displays a distorted tetrahedral coordinated sphere with six angles ranging from $96.00(12)^\circ$ to

$116.36(15)^\circ$. The Sn–C bond lengths [$2.119(4)$ – $2.1231(3)$ Å] are consistent with those reported in other triorganotin carboxylates [36,37]. The Sn(2)–O(3) distance [$2.060(2)$ Å] is little shorter than reported in [$\text{Ph}_3\text{Sn}(\text{O}_2\text{CC}_6\text{H}_5)$] (2.073 Å) [38] and approaches the sum of the covalent radii of Sn and O (2.13 Å) [39], but much shorter than the sum of the van der Waals radii of Sn and O (3.68 Å) [39]. The other center tin atom is rendered five-coordinated by coordinating with the nitrogen atom. The tin atom is rendered a distorted trigonal bipyramidal type, surrounded axially by one oxygen atom, one nitrogen atom and equatorially by three carbon atoms of the phenyl groups. The O and N atoms occupying the axial sites [Sn(1)–O(1) $2.117(2)$, Sn(1)–N($1^{\wedge}1^{\wedge}$) $2.711(3)$ Å and O(1)–Sn(1)–N($1^{\wedge}1^{\wedge}$) $174.45(9)^\circ$] (symmetry code: $x - 1/2, -y + 1/2, z - 1/2$). Despite the rather high estimated standard deviations in the C–O bond distances a clear trend in these parameters may be discerned. As expected the C–O bond distances [C(6)–O(2) $1.213(4)$ Å, C(7)–O(4) $1.211(4)$ Å] associated with the non-coordinating O atoms are significantly shorter than the coordinating C–O bond distances [C(6)–O(1) $1.293(4)$ Å, C(7)–O(3) $1.310(4)$ Å]. Furthermore, it is noteworthy that a weak intermolecular Sn...O interaction is recognized between the Sn(1) and O(2), Sn(2) and O(4) [O(2) and O(4) derived of the monodentate carboxyl group. The Sn(1)...O(2) distance [$3.086(3)$ Å] and Sn(2)...O(4) distance [$2.919(3)$ Å] which are shorter than in **1** [3.540 Å] and are considerably less than the sum of the van der Waals radii (3.68 Å). Thus, if the weak Sn...O interaction is considered, the geometry of Sn(1) is best described as distorted octahedron (see Fig. 6).

The 1D supramolecular structure of complex **5** is formed via the intermolecular Sn...N interactions. The Sn...N bond distance Sn(1)...N($1^{\wedge}1^{\wedge}$) is $2.711(3)$ Å is greater than the sum of the covalent radii of Sn and N (2.15 Å), but is considerably less than the sum of the van der Waals radii (3.75 Å) [39] and should be considered as bonding interaction. The angles of O(1)–Sn(1)–N($1^{\wedge}1^{\wedge}$) is $174.45(9)^\circ$, which deviates from linear angle 180° . These data indicate that the five-coordinated tin atom is distorted trigonal bipyramidal geometry (see Table 3).

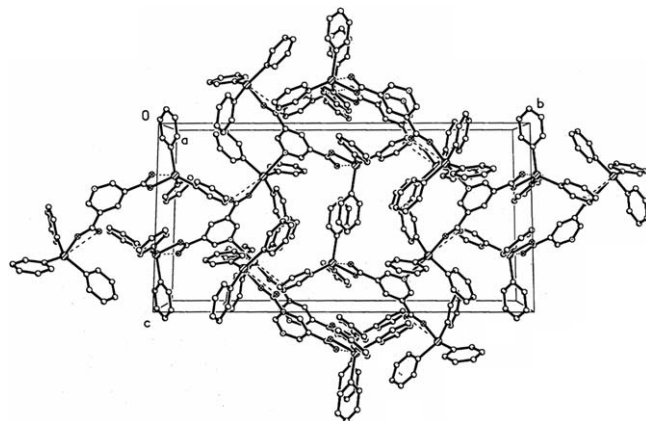
Fig. 6. The packing diagram of **5**.

Table 3
Selected bond lengths (Å) and angles (°) for complex 5

Bond lengths		Bond angles	
Sn(1)–O(1)	2.117(2)	O(1)–Sn(1)–C(14)	101.11(11)
Sn(1)–C(14)	2.119(3)	O(1)–Sn(1)–C(20)	89.56(11)
Sn(1)–C(20)	2.127(4)	O(1)–Sn(1)–C(8)	96.18(12)
Sn(1)–C(8)	2.129(4)	O(1)–Sn(1)–N(1 [^])	174.45(9)
Sn(1)–N(1 [^])	2.711(3)	O(1)–Sn(1)–O(2)	46.15(8)
Sn(1)–O(2)	3.086(3)	C(14)–Sn(1)–O(2)	75.25(11)
Sn(2)–O(3)	2.060(2)	N(1 [^])–Sn(1)–O(2)	138.17(8)
Sn(2)–C(38)	2.119(4)	O(3)–Sn(2)–C(38)	110.13(12)
Sn(2)–C(32)	2.129(4)	O(3)–Sn(2)–C(32)	106.52(12)
Sn(2)–C(26)	2.131(3)	C(38)–Sn(2)–C(32)	116.36(15)
Sn(2)–O(4)	2.919(3)	O(3)–Sn(2)–C(26)	96.00(12)
O(1)–C(6)	1.293(4)	O(38)–Sn(2)–C(26)	113.85(14)
O(2)–C(6)	1.213(4)	C(32)–Sn(2)–C(26)	111.77(14)
O(4)–C(7)	1.211(4)	O(3)–Sn(2)–O(4)	49.43(8)

Symmetry code: $\hat{1}^{\wedge} x - 1/2, -y + 1/2, z - 1/2$.

2.4.3. $[(Me_3Sn)_2(2,5-pdc)]_n$ (7)

The molecular structure and cyclic unit are illustrated in Figs. 7 and 8, respectively. It consists of infinite ribbons extending through the cell in the *c* direction, as indicated in Fig. 9. Bond lengths and bond angles are given in Table 4. The trimethyltin(IV) groups are linked by a carboxylate of each pdc ligand in 7, in turn, employs its two bidentate carboxylic groups to coordinate to four metal centers. Thus, four ligands are linked by four metal centers into a 24-membered macrocycle and this can be seen from Fig. 8, which is further linked to eight nearest-neighbor tin centers by four independent pdc ligands to give rise to a lattice 2D network with a cavity that can be evaluated by the Sn···Sn and transannular O···O distances, which are

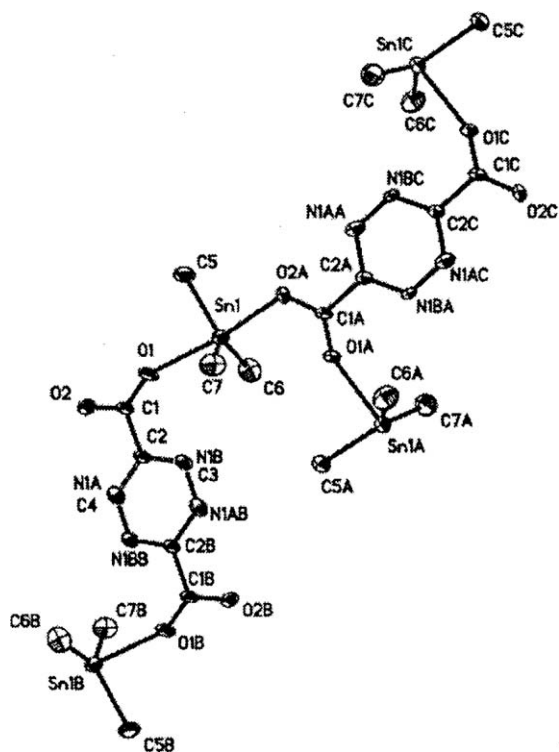


Fig. 7. Molecular structure of 7.

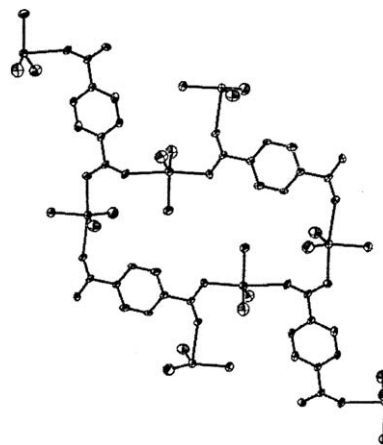


Fig. 8. The 24-membered unit of 7.

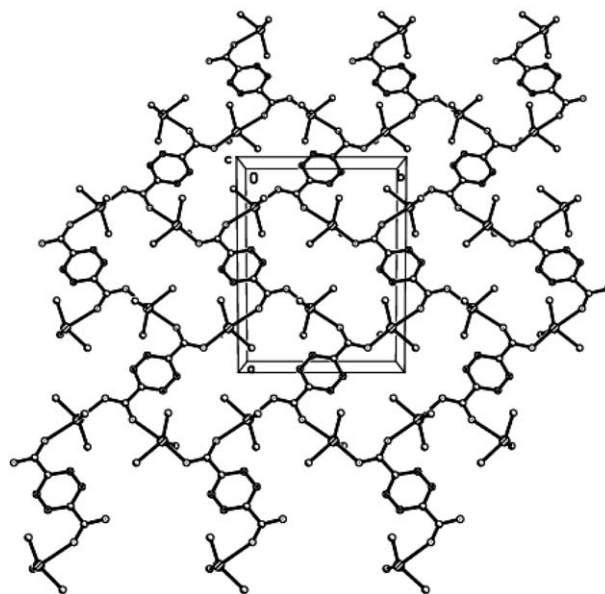


Fig. 9. The unit cell show network structure of 7.

Table 4
Selected bond lengths (Å) and angles (°) for complex 7

Bond lengths		Bonds angles	
Sn(1)–C(7)	2.081(10)	C(7)–Sn(1)–C(6)	126.6(5)
Sn(1)–C(6)	2.082(10)	C(7)–Sn(1)–C(5)	116.6(5)
Sn(1)–C(5)	2.103(10)	C(6)–Sn(1)–C(5)	115.9(5)
Sn(1)–O(2 [^] 1 [^])	2.181(5)	O(2 [^] 1 [^])–Sn(1)–O(1)	172.9(2)
Sn(1)–O(1)	2.421(6)	C(1)–O(1)–Sn(1)	153.1(6)
O(1)–C(1)	1.234(9)	C(1)–O(2)–Sn(1 [^] 2 [^])	121.9(5)
O(2)–C(1)	1.259(10)	O(1)–C(1)–O(2)	126.5(8)
C(1)–C(2)	1.528(11)	N(1A)–C(2)–N(1B)	120.8(8)
C(2)–N(1A)	1.341(9)	N(1A)–C(2)–C(1)	118.9(7)
C(2)–N(1B)	1.381(11)	C(2)–N(1A)–N(1B [^] 3 [^])	117.7(7)
N(1A)–N(1B [^] 3 [^])	1.361(12)	N(1A [^] 3 [^])–N(1B)–C(2)	121.5(7)

Symmetry code: $\hat{1}^{\wedge} -x + 1/2, y + 1/2, -z + 1/2$; $\hat{2}^{\wedge} -x + 1/2, y - 1/2, -z + 1/2$.

7.497–13.314 and 6.137–13.590 Å, respectively. Similar cavities have been found within the polymeric crystal structures of microporous metal-organic frameworks formed between 1,3,5-benzenetricarboxylic acid and Sn [40], Co

[41] centers. In other related polymeric systems so far only dimeric [42], hexameric [43], and chainlike [44] motifs have been reported.

All the tin atoms in **7** possess a same coordination environment. The coordination about the tin atom is only slightly distorted from the regular trigonal bipyramidal geometry. Associated with the Sn(1)–O(2¹) (symmetry code: $-x + 1/2, y + 1/2, -z + 1/2$) distance [2.181(5) Å] is a little longer than reported in [Me₃Sn(O₂CC₄H₃S)] (2.149 Å) [45]. The Sn(1)–O(1) distance [2.421(6) Å] is close to the distance between coordinated O atom and central tin atom in other organotin complexes [15], but much shorter than the sum of the van der Waals radii of Sn and O (3.68 Å). The angle O(1)–Sn(1)–O(2¹) 172.9(2)° is close to a linear arrangement. The sum of the angles subtended at the tin atom in the equatorial plane is 359.3(5) for Sn(1), so that the atoms Sn(1), C(5), C(6) and C(7) are almost in the same plane. The Sn–C distances [2.081(10)–2.103(10) Å] are equal within experimental error and close to the single-bond value for trigonal bipyramidal tin [39]. The pyridine ring is centered on a crystallographic center of symmetry (1/2, 1, 1/2) coincides with its centroid. Thus, it is disordered and the N atom is in any one of the four sites, C(3), C(4) and their symmetric atoms. This case is shown in Fig. 7.

3. Experimental details

3.1. Materials and measurements

Trimethyltin chloride, triphenyltin chloride, 2,6-pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid and 2,5-pyridinedicarboxylic acid were commercially available, and they were used without further purification. Tribenzyltin(IV) chloride was prepared by a standard method reported in the literature [46]. The melting points were obtained with Kofler micro melting point apparatus and are uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on 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; ¹³C spectra are broadband proton decoupled. The chemical shifts are reported in ppm with respect to the references and are stated relative to external tetramethylsilane (TMS) for ¹H and ¹³C NMR and Me₄Sn for ¹¹⁹Sn NMR. Elemental analyses were performed with a PE-2400II apparatus.

3.2. Syntheses

The general route of synthesis is shown in the following. The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. Dicarboxylic acids (2,6-pyridinedicarboxylic acid 3,5-pyridinedicarboxylic acid or 2,5-pyridinedicarboxylic acid) (1.0 mmol) and the triethylamine (2.0 mmol) were added to the solution of benzene, the mixture was stirred for 10 min, then triorganotin

chlorides (1.0 mmol) was added to the mixture, continuing the reaction for about 12 h at 40 °C. After cooling down to room temperature, the precipitate was filtered off. The solids of **1–9** were then recrystallized from hexane–dichloromethane to give colorless crystals. Interestingly, coordinated water molecules were found in complexes **1–3** and this may be caused by the recrystallization procedure.

3.2.1. [(C₂H₅)₃NH][Me₃Sn]₃(2,6-pdc)₂(H₂O)₂ (**1**)

Yield: 85%; m.p. 160–162 °C. Anal. Found: C, 36.26; H, 5.56; N, 4.40. Calc. for C₂₉H₅₃N₃O₁₀Sn₃: C, 36.29; H, 5.57; N, 4.38%. IR (KBr, cm⁻¹): ν(H–O–H), 3327; ν_{as}(COO), 1623; ν_s(COO), 1309; ν(Sn–O), 483. ¹H NMR (CDCl₃, 400 MHz ppm): δ = 8.98 (s, H₂O); 7.68–8.26 (pyridine); 3.17 (m, 6H, N-CH₂CH₃); 1.37 (t, 9H, N-CH₂CH₃); 0.82 (s, 27H, CH₃). ¹³C NMR (CDCl₃, 100.6 ppm): δ = 11.8 (m, CH₃), 173.8 (COO), pyridyl: 145.9 (C_o), 127.3 (C_m), 136.2 (C_p). ¹¹⁹Sn NMR (CDCl₃, 149.2 MHz ppm): –112.

3.2.2. [(C₂H₅)₃NH][Ph₃Sn]₃(2,6-pdc)₂(H₂O)₂ (**2**)

Yield: 82%; m.p. 172–174 °C. Anal. Found: C, 58.52; H, 4.73; N, 2.78. Calc. for C₇₄H₇₁N₃O₁₀Sn₃: C, 58.53; H, 4.71; N, 2.77%. IR (KBr, cm⁻¹): ν(H–O–H), 3325; ν_{as}(COO), 1625; ν_s(COO), 1305; ν(Sn–O), 485. ¹H NMR (CDCl₃, 400 MHz ppm): δ = 8.97 (s, H₂O); 7.62–8.22 (pyridine); 3.16 (m, 6H, N-CH₂CH₃); 1.35 (t, 9H, N-CH₂CH₃); 7.46–7.79 (m, 45H, Ph). ¹³C NMR (CDCl₃, 100.6 ppm): δ = 128.8–137.5 (Ph), 173.5 (COO), pyridyl: 147.3 (C_o), 128.2 (C_m), 138.8 (C_p). ¹¹⁹Sn NMR (CDCl₃, 149.2 MHz ppm): –122.

3.2.3. [(C₂H₅)₃NH]{[PhCH₂]₃Sn}₃(2,6-pdc)₂(H₂O)₂ (**3**)

Yield: 85%; m.p. 178–180 °C. Anal. Found: C, 60.60; H, 5.47; N, 2.53. Calc. for C₈₃H₈₉N₃O₁₀Sn₃: C, 60.61; H, 5.45; N, 2.55%. IR (KBr, cm⁻¹): ν(H–O–H), 3320; ν_{as}(COO), 1630; ν_s(COO), 1312; ν(Sn–O), 487. ¹H NMR (CDCl₃, 400 MHz ppm): δ = 8.95 (s, H₂O); 7.75–8.35 (pyridine); 3.15 (m, 6H, N-CH₂CH₃); 1.35 (t, 9H, N-CH₂CH₃); 2.6 (s, 18H, CH₂Ph); 7.06–7.14 (m, 45H, Ph). ¹³C NMR (CDCl₃, 100.6 ppm): δ = 10.6 (m, CH₂Ph), 125.8–142.8 (Ph), 173.6 (COO), pyridyl: 146.2 (C_o), 126.4 (C_m), 136.2 (C_p). ¹¹⁹Sn NMR (CDCl₃, 149.2 MHz ppm): –118.

3.2.4. [Me₃Sn(3,5-pdc)]_n (**4**)

Yield: 79%; m.p. 106–108 °C. Anal. Found: C, 36.51; H, 3.70; N, 4.25. Calc. for C₁₀H₁₂NO₄Sn: C, 36.52; H, 3.68; N, 4.26%. IR (KBr, cm⁻¹): ν_{as}(COO), 1615; ν_s(COO), 1312; ν(Sn–O), 485. ¹H NMR (CDCl₃, 400 MHz ppm): δ = 0.9 (s, 18H, CH₃); 7.85, 8.45 (pyridine). ¹³C NMR (CDCl₃, 100.6 ppm): δ = 4.9, 11.5 (CH₃), 171.6 (COO), pyridine: 153.0 (C_o), 126.9 (C_m), 138.8 (C_p). ¹¹⁹Sn NMR (CDCl₃, 149.2 MHz ppm): –85.

3.2.5. [Ph₃Sn(3,5-pdc)]_n (**5**)

Yield: 78%; m.p. 100–102 °C. Anal. Found: C, 58.27; H, 3.54; N, 2.71. Calc. for C₂₅H₁₈NO₄Sn: C, 58.29; H, 3.52; N,

2.72%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1617; $\nu_{\text{s}}(\text{COO})$, 1315; $\nu(\text{Sn-O})$, 489. ^1H NMR (CDCl_3 , 400 MHz ppm): $\delta = 7.76\text{--}8.32$ (pyridine); 7.26–7.49 (15H, Ph). ^{13}C NMR (CDCl_3 , 100.6 ppm): $\delta = 170.7$ (COO), pyridine: 152.6 (C_o), 124.9 (C_m), 138.8 (C_p). ^{119}Sn NMR (CDCl_3 , 149.2 MHz ppm): -87 .

3.2.6. $[(\text{PhCH}_2)_3\text{Sn}(3,5\text{-pdc})]_n$ (**6**)

Yield: 76%; m.p. 124–126 °C. Anal. Found: C, 60.34; H, 4.36; N, 2.50. Calc. for $\text{C}_{28}\text{H}_{24}\text{NO}_4\text{Sn}$: C, 60.35; H, 4.34; N, 2.51%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1619; $\nu_{\text{s}}(\text{COO})$, 1318; $\nu(\text{Sn-O})$, 487. ^1H NMR (CDCl_3 , 400 MHz ppm): $\delta = 7.66\text{--}8.12$ (pyridine); 7.26–7.49 (15H, Ph). ^{13}C NMR (CDCl_3 , 100.6 ppm): $\delta = 171.2$ (COO), pyridine: 153.1 (C_o), 125.2 (C_m), 137.5 (C_p). ^{119}Sn NMR (CDCl_3 , 149.2 MHz ppm): -88 .

3.2.7. $[(\text{Me}_3\text{Sn})_2(2,5\text{-pdc})]_n$ (**7**)

Yield: 83%; m.p. 198–200 °C. Anal. Found: C, 31.61; H, 4.46; N, 2.86. Calc. for $\text{C}_{13}\text{H}_{21}\text{NO}_4\text{Sn}_2$: C, 31.62; H, 4.49; N, 2.84%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1618; $\nu_{\text{s}}(\text{COO})$, 1433; $\nu(\text{Sn-O})$, 478. ^1H NMR (CDCl_3 , 400 MHz ppm): $\delta = 1.01$ (s, CH_3 , 18H); 7.45–7.85 (pyridine). ^{13}C NMR (CDCl_3 , 100.6 ppm): $\delta = 14.1$ (s, CH_3), 172.1 (COO), pyridine: 150.4, 151.3 (C_o), 124.6, 130.9 (C_m), 139.1 (C_p). ^{119}Sn NMR (CDCl_3 , 149.2 MHz ppm): -115 .

3.2.8. $[(\text{Ph}_3\text{Sn})_2(2,5\text{-pdc})]_n$ (**8**)

Yield: 83%; m.p. >220 °C. Anal. Found: C, 59.55; H, 4.10; N, 1.60. Calc. for $\text{C}_{43}\text{H}_{35}\text{NO}_4\text{Sn}_2$: C, 59.56; H, 4.07; N, 1.62%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1620; $\nu_{\text{s}}(\text{COO})$, 1436; $\nu(\text{Sn-O})$, 481. ^1H NMR (CDCl_3 , 400 MHz ppm): $\delta = 7.28\text{--}7.51$ (15H, Ph); 7.56–7.95 (pyridine). ^{13}C NMR (CDCl_3 , 100.6 ppm): $\delta = 171.15$ (COO), pyridine: 151.2, 151.8 (C_o), 123.5, 129.4 (C_m), 137.8 (C_p). ^{119}Sn NMR (CDCl_3 , 149.2 MHz ppm): -118 .

3.2.9. $\{[(\text{PhCH}_2)_3\text{Sn}]_2(2,5\text{-pdc})\}_n$ (**9**)

Yield: 84%; m.p. 208–210 °C. Anal. Found: C, 61.84; H, 4.99; N, 1.46. Calc. for $\text{C}_{49}\text{H}_{47}\text{NO}_4\text{Sn}_2$: C, 61.86; H, 4.98; N, 1.47%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1617; $\nu_{\text{s}}(\text{COO})$, 1431; $\nu(\text{Sn-O})$, 479. ^1H NMR (CDCl_3 , 400 MHz ppm): $\delta = 2.5$ (s, 12H, CH_2Ph); 7.06–7.14 (m, 30H, Ph); 7.65–7.98 (pyridine). ^{13}C NMR (CDCl_3 , 100.6 ppm): $\delta = 172.0$ (COO), pyridine: 150.5, 151.7 (C_o), 121.5, 126.4 (C_m), 136.0 (C_p). ^{119}Sn NMR (CDCl_3 , 149.2 MHz ppm): -117 .

3.3. X-ray crystallographic studies

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Smart CCD area-detector with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full matrix least-squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crys-

tal data and experimental details of the structure determinations are listed in Table 1.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis of complexes **1**, **5** and **7** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 269145 (**1**), 283416 (**5**) and 283417 (**7**). Copies of these information may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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