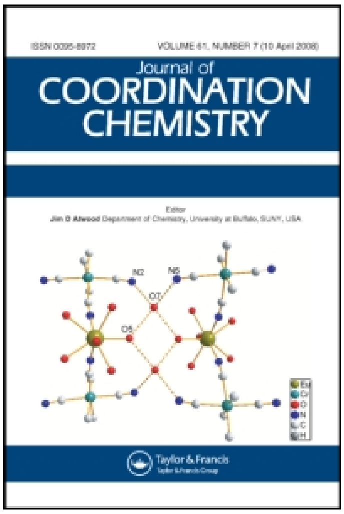

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Syntheses and crystal structures of polymeric ionic triorganotin esters of 3,5-pyridinedicarboxylic acid and 5-nitroisophthalic acid

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The triethylammonium dicarboxylatotriorganostannates, $[(C_2H_5)_3NH][R_3Sn(3,5\text{-pdc})] \cdot mH_2O$ (3,5-pdc = 3,5-pyridinedicarboxylate) ($m = 1$, R = Me **1**; $m = 0$, R = Ph **2**, $PhCH_2$ **3**, *n*-Bu **4**), $[(C_2H_5)_3NH][R_3Sn(5\text{-nip})]$ (5-nip = 5-nitroisophthalate) (R = Me **5**, Ph **6**, $PhCH_2$ **7**, *n*-Bu **8**) have been prepared from triethylamine, 3,5-pyridinedicarboxylic acid, 5-nitroisophthalic acid and triorganotin chloride. Complexes **1**–**8** have been characterized by elemental, IR, ^1H, ^{13}C and ^{119}Sn NMR analyses. Complexes **1**, **2**, **5** and **6** are also determined by single crystal X-ray diffraction. For **1**, **2**, **5** and **6**, each carboxylate moiety is involved in coordination to a tin center via only one O atom showing that the Sn atoms are five-coordinate and exist in trigonal bipyramidal geometries. Moreover, for **2**, **5** and **6**, the nitrogen atoms of ammonium are hydrogen bonded to the pendant carboxyl oxygen. In **1**, adjacent polymeric chains and triethylammonium are linked by hydrogen bonds through the co-crystallized water molecule, thus a 2D network is formed.

Keywords: Dicarboxylic acid; Triorganotin; Hydrogen bond; Crystal structure; X-ray crystallography

1. Introduction

Organotin(IV) carboxylates have attracted attention owing to their potential biocidal activities [1–4] and cytotoxicities [5] as well as their industrial and agricultural applications [6–11]. 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 been undertaken on the triorganotin esters of dicarboxylic acids [21–24]. In the case of bis(triorganotin) esters of dicarboxylic acids, the presence of an additional carboxyl group gives rise to 3D networks [25, 26]. Structures of some dicyclohexylammonium mono(triorganotin)dicarboxylates have been reported. In 2,6-pyridinedicarboxylatotributylstannate, the dicarboxylato group links the triorganotin groups into a polymeric linear infinite chain [27], similar to succinatotriphenylstannate [28].

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In our previous studies, a linear infinite chain was also obtained by the synthesis and crystal structure of polymeric triethylammonium 2,5-thiophenedicarboxylatotriphenylstannate [29]. In tris(oxalato)tetrakis(tributylstannate), two oxalatotributylstannate anions flank a bis(tributyltin) oxalate molecule to form a short tetranuclear chain [30]. The structure of tris(malonato)tetrakis(tributylstannate) contains a centrosymmetric tetranuclear dianion [31].

In order to extend the work in this field, we synthesized the triethylammonium dicarboxylatotriorganostannates, $[(C_2H_5)_3NH][R_3Sn(3,5\text{-pdc})]\cdot mH_2O$ (3,5-pdc = 3,5-pyridinedicarboxylate) ($m=1$, R = Me **1**; $m=0$, R = Ph **2**, $PhCH_2$ **3**, *n*-Bu **4**), $[(C_2H_5)_3NH][R_3Sn(5\text{-nip})]$ (R = Me **5**, Ph **6**, $PhCH_2$ **7**, *n*-Bu **8**) from triethylamine, 3,5-pyridinedicarboxylic acid, 5-nitroisophthalic acid and triorganotin chloride. Complexes **1**–**8** have been characterized by elemental, IR, ^1H, ^{13}C and ^{119}Sn NMR analyses and complexes **1**, **2**, **5** and **6** were also determined by single X-ray diffractions.

2. Experimental

2.1. *Materials and measurements*

Trimethyltin chloride, triphenyltin chloride, tri-*n*-butyltin chloride, 3,5-pyridinedicarboxylic acid and 5-nitroisophthalic acid were commercially available and used without further purification. Tribenzyltin chloride was prepared by a standard method reported in the literature [39]. The melting points were obtained with a 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, ^{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; ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in ppm with respect to the references, external tetramethylsilane (TMS) for ^1H and ^{13}C NMR and Me_4Sn for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400II apparatus.

2.2. *Syntheses*

The general synthesis is shown in the following. The reaction was carried out under nitrogen with use of standard Schlenk techniques. Dicarboxylic acids (3,5-pyridinedicarboxylic acid and 5-nitroisophthalic acid) (1.0 mmol) and the triethylamine (2.0 mmol) were added to benzene and the mixture was stirred for 10 min. Then triorganotin chloride (1.0 mmol) was added to the mixture, continuing the reaction for about 12 h at 40°C. After cooling to room temperature, the precipitate was filtered off. The solid was then recrystallized from methanol giving colorless crystals.

2.2.1. Synthesis of $[(C_2H_5)_3NH][Me_3Sn(3,5\text{-pdc})]\cdot mH_2O$ (1). Yield: 81%, m.p. 178–180°C. Anal. Found: C, 42.75; H, 6.71; N, 6.25. Calcd for $C_{16}H_{30}N_2O_5Sn$: C, 42.79; H, 6.73; N, 6.24%. IR (KBr, cm^{-1}): ν(H–O–H), 3500; ν_{as}(COO), 1617; ν_s(COO), 1305; ν(Sn–O), 476. ^1H NMR ($CDCl_3$, 400 MHz ppm): δ 9.30 (s, 2H, H_2O);

7.28, 8.45 (pyridine); 3.15 (m, 6H, N–CH_2CH_3); 1.25 (t, 9H, N–CH_2CH_3); 0.74 (s, 9H, Sn–CH_3). ^{13}C NMR ($CDCl_3$, 100.6 ppm): δ 171.62 (COO), pyridine: 152.96 (C2, C6) 127.90 (C3, C5), 137.82 (C4), 8.60 (CH_3). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz ppm): -105.

2.2.2. Synthesis of [$(C_2H_5)_3NH$][Ph_3Sn(3,5-pdc)] (2). Yield: 78%, m.p. > 220°C. Anal. Found: C, 60.30; H, 5.52; N, 4.56. Calcd for $C_{31}H_{34}N_2O_4Sn$: C, 60.31; H, 5.55; N, 4.54%. IR (KBr, cm^{-1}): ν_{as}(COO), 1617; ν_s(COO), 1305; ν(Sn–O), 489. ^{1}H NMR ($CDCl_3$, 400 MHz ppm): δ 7.55, 8.95 (pyridine); 7.36–7.79 (15H, Ph); 3.15 (m, 6H, N–CH_2CH_3); 1.30 (t, 9H, N–CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100.6 ppm): δ 170.75 (COO), pyridine: 153.67 (C2, C6), 128.96 (C3, C5), 138.83 (C4), 128.2 (*m*-C), 129.3 (*p*-C), 136.7 (*o*-C), 142.6 (*i*-C). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz ppm): -102.

2.2.3. Synthesis of [$(C_2H_5)_3NH$][$(PhCH_2)_3Sn$(3,5-pdc)] (3). Yield: 83%, m.p. 170–172°C. Anal. Found: C, 61.91; H, 6.10; N, 4.26. Calcd for $C_{34}H_{40}N_2O_4Sn$: C, 61.93; H, 6.11; N, 4.25%. IR (KBr, cm^{-1}): ν_{as}(COO), 1618; ν_s(COO), 1310; ν(Sn–O), 478. ^{1}H NMR ($CDCl_3$, 400 MHz ppm): δ 7.45, 8.55 (pyridine); 7.46–7.79 (m, 15H, Ph); 3.26 (6H, CH_2–Ph); 3.20 (m, 6H, N–CH_2CH_3); 1.35 (t, 9H, N–CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100.6 ppm): δ 171.85 (COO), pyridine: 150.55 (C2, C6), 125.95 (C3, C5), 136.80 (C4), 127.4 (*m*-C), 128.2 (*p*-C), 127.3 (*o*-C), 124.2 (*i*-C). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz ppm): -108.

2.2.4. Synthesis of [$(C_2H_5)_3NH$][(n-Bu)$_3$Sn(3,5-pdc)] (4). Yield: 83%, m.p. 166–168°C. Anal. Found: C, 53.86; H, 8.30; N, 5.05. Calcd for $C_{25}H_{46}N_2O_4Sn$: C, 53.87; H, 8.32; N, 5.03%. IR (KBr, cm^{-1}): ν_{as}(COO), 1615; ν_s(COO), 1305; ν(Sn–O), 484. ^{1}H NMR ($CDCl_3$, 400 MHz ppm): δ 7.18, 8.35 (pyridine); 3.15 (m, 6H, N–CH_2CH_3); 1.25 (t, 9H, N–CH_2CH_3); 1.26–1.75 (18H); 0.89 (t, 9H). ^{13}C NMR ($CDCl_3$, 100.6 ppm): δ 172.62 (COO), pyridine: 151.95 (C2, C6), 126.95 (C3, C5), 136.85 (C4), 13.6, 26.4, 27.6, 29.7 (*n*-Bu). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz ppm): -110.

2.2.5. Synthesis of [$(C_2H_5)_3NH$][$Me_3Sn(O_2C)C_6H_3(NO_2)$] (5). Yield: 85%, m.p. 158–160°C. Anal. Found: C, 42.95; H, 5.93; N, 5.91. Calcd for $C_{17}H_{28}N_2O_6Sn$: C, 42.97; H, 5.94; N, 5.90%. IR (KBr, cm^{-1}): ν_{as}(COO), 1624; ν_s(COO), 1325; ν(Sn–O), 475. ^{1}H NMR ($CDCl_3$, 400 MHz ppm): δ 7.80–6.92 (m, aryl); 3.15 (m, 6H, N–CH_2CH_3); 1.25 (t, 9H, N–CH_2CH_3); 0.71 (s, 9H, Sn–CH_3). ^{13}C NMR ($CDCl_3$, 100.6 ppm): δ 171.91 (COO), 162.96, 137.82, 126.17 (aryl); 8.59 (CH_3). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz ppm): -98.

2.2.6. Synthesis of [$(C_2H_5)_3NH$][$Ph_3Sn(O_2C)C_6H_3(NO_2)$] (6). Yield: 78%, m.p. > 220°C. Anal. Found: C, 58.11; H, 5.16; N, 4.25. Calcd for $C_{32}H_{34}N_2O_6Sn$: C, 58.12; H, 5.18; N, 4.24%. IR (KBr, cm^{-1}): ν_{as}(COO), 1624; ν_s(COO), 1325; ν(Sn–O), 480. ^{1}H NMR ($CDCl_3$, 400 MHz ppm): δ 7.30–7.90 (m, aryl and Ph); 3.15 (m, 6H, N–CH_2CH_3); 1.36 (t, 9H, N–CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100.6 ppm): δ 172.60 (COO), 160.96–129.00 (aryl); 128.2 (*m*-C), 129.3 (*p*-C), 136.7 (*o*-C), 142.6 (*i*-C). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz ppm): -95.

2.2.7. Synthesis of $[(C_2H_5)_3NH][(PhCH_2)_3Sn(O_2C)C_6H_3(NO_2)]$ (7). Yield: 81%, m.p. 120–122°C. Anal. Found: C, 59.75; H, 5.71; N, 3.99. Calcd for $C_{35}H_{40}N_2O_6Sn$: C, 59.76; H, 5.73; N, 3.98%. IR (KBr, cm^{-1}): ν_{as}(COO), 1624; ν_s(COO), 1325; ν(Sn–O), 482. ^{1}H NMR ($CDCl_3$, 400 MHz ppm): δ 7.30–7.89 (m, aryl and Ph); 3.26 (6H, CH_2–Ph); 3.15 (m, 6H, N–CH_2CH_3); 1.36 (t, 9H, N–CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100.6 ppm): δ 173.65 (COO), 161.15–130.00 (aryl); 127.4 (*m*-C), 128.2 (*p*-C), 127.3 (*o*-C), 124.2 (*i*-C). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz ppm): −93.

2.2.8. Synthesis of $[(C_2H_5)_3NH][(n\text{-}Bu)_3Sn(O_2C)C_6H_3(NO_2)]$ (8). Yield: 82%, m.p. 170–172°C. Anal. Found: C, 51.90; H, 7.70; N, 4.68. Calcd for $C_{26}H_{46}N_2O_6Sn$: C, 51.93; H, 7.71; N, 4.66%. IR (KBr, cm^{-1}): ν_{as}(COO), 1624; ν_s(COO), 1325; ν(Sn–O), 490. ^{1}H NMR ($CDCl_3$, 400 MHz ppm): δ 7.90, 7.15 (m, aryl); 3.15 (m, 6H, N–CH_2CH_3); 1.25 (t, 9H, N–CH_2CH_3); 1.25–1.75 (18H); 0.92 (t, 9H). ^{13}C NMR ($CDCl_3$, 100.6 ppm): δ 172.52 (COO), 126.17–162.96 (aryl); 13.5, 26.5, 27.5, 30.1 (*n*-Bu). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz ppm): −97.

2.3. *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-Kα 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. Crystal data and experimental details of the structure determinations are listed in table 1.

3. Results and discussion

3.1. *Syntheses aspects*

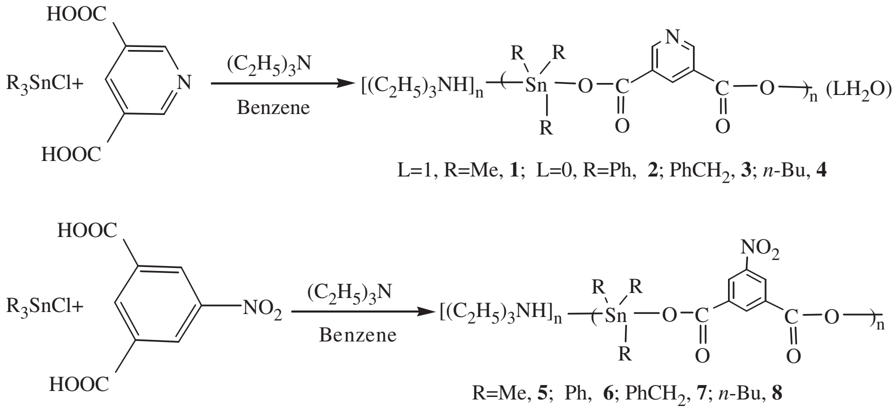
The triethylammonium dicarboxylatotriorganostannates, $[(C_2H_5)_3NH][Me_3Sn(3,5\text{-}pdc)] \cdot mH_2O$ (3,5-pdc = 3,5-pyridinedicarboxylate) ($m = 1$, R = Me **1**; $m = 0$, R = Ph **2**, $PhCH_2$ **3**, *n*-Bu **4**) and $[(C_2H_5)_3NH][R_3Sn(5\text{-}nip)]$ (R = Me **5**, Ph **6**, $PhCH_2$ **7**, *n*-Bu **8**) have been prepared from triethylamine, 3,5-H_2pdc, 5-nitroisophthalic and triorganotin chloride. The syntheses procedure is given in scheme 1.

3.2. *Spectroscopic studies*

3.2.1. IR spectroscopy. The infrared spectrum of the two free ligands show ν(C=O) of COOH at 1667 and 1691 cm^{-1}, respectively, as a strong band, indicating that intermolecular hydrogen bonding of the type C=O···H–O exists in the uncoordinated 3,5-pyridinedicarboxylic acid and 5-nitroisophthalic acid molecules. This is commonly observed in the case of carboxylic acids [32]. After deprotonation and coordination to Sn, these bands disappear and are replaced by strong bands in the 1580–1630 and 1320–1330 cm^{-1} regions, which correspond to the asymmetric and symmetric vibrations, respectively, of the COO moiety. Strong absorptions appear

Table 1. Crystal, data collection and structure refinement parameters for complexes **1**, **2**, **5** and **6**.

Complex	**1**	**2**	**5**	**6**
Empirical formula	$C_{16}H_{30}N_2O_5Sn$	$C_{31}H_{34}N_2O_4Sn$	$C_{17}H_{28}N_2O_6Sn$	$C_{32}H_{34}N_2O_6Sn$
Formula weight	449.11	617.29	475.10	661.33
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/n$	$P2_1/c$
a (Å)	7.7852(1)	16.527(2)	7.437(3)	10.5179(9)
b (Å)	20.708(3)	17.889(2)	20.691(3)	16.3427(1)
c (Å)	12.808(2)	19.911(2)	13.607(3)	20.1897(1)
α (°)	90	90	90	90
β (°)	98.905(2)	90	99.070(3)	118.725(3)
γ (°)	90	90	90	90
Z	4	8	4	4
D_{calcd} (Mg m^{-3})	1.462	1.393	1.526	1.448
$F(000)$	920	2528	968	1356
μ (mm^{-1})	1.277	0.905	1.268	0.886
Crystal size (mm^3)	0.44 × 0.37 × 0.21	0.53 × 0.37 × 0.32	0.43 × 0.25 × 0.21	0.30 × 0.20 × 0.18
θ range (°)	1.89–25.03	2.39–25.08	1.81–25.03	1.70–27.50
Index ranges	$-9 \le h \le 9$; $-24 \le k \le 16$; $-14 \le l \le 15$	$-13 \le h \le 19$; $-21 \le k \le 21$; $-23 \le l \le 23$	$-8 \le h \le 8$; $-18 \le k \le 24$; $-16 \le l \le 16$	$-13 \le h \le 13$; $-21 \le k \le 21$; $-26 \le l \le 26$
Reflections collected	10,628	25,468	10,691	34,389
Unique reflections	3605 ($R_{int} = 0.0347$)	5134 ($R_{int} = 0.1197$)	3646 ($R_{int} = 0.0345$)	6973 ($R_{int} = 0.0301$)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squivalantson F^2	Full-matrix least-squivalants on F^2	Full-matrix least-squivalants on F^2	Full-matrix least-squivalants on F^2
Data/restraints/parameters	3605/3/223	5134/6/343	3646/12/262	6973/0/370
Goodness of fit on F^2	1.000	1.003	1.004	1.003
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0342$, $wR_2 = 0.0966$	$R_1 = 0.0464$, $wR_2 = 0.1152$	$R_1 = 0.0369$, $wR_2 = 0.1029$	$R_1 = 0.0347$, $wR_2 = 0.0904$
R indices (all data)	$R_1 = 0.0484$, $wR_2 = 0.1056$	$R_1 = 0.0868$, $wR_2 = 0.1493$	$R_1 = 0.0537$, $wR_2 = 0.1519$	$R_1 = 0.0420$, $wR_2 = 0.0961$



L=1, R=Me, **1**; L=0, R=Ph, **2**; PhCH$_2$, **3**; *n*-Bu, **4**

R=Me, **5**; Ph, **6**; PhCH$_2$, **7**; *n*-Bu, **8**

Scheme 1. The synthesis procedure of complexes **1–8**.

at 474–492 cm^{-1} in the spectra of complexes **1–8**, which are absent in the spectra of the free ligands, are assigned to the Sn–O stretching mode of vibration. All these values are consistent with a number of organotin(IV) derivatives [33–35]. In **1**, the presence of water molecules is indicted by the peak at ca 3500 cm^{-1} in the infrared spectrum.

IR spectra provides useful information concerning the coordination of the carboxyl. The magnitude of $\Delta\nu$ ($\nu_{as}(COO^-) - \nu_{sym}(COO^-)$) at 315 cm^{-1} for complexes **1–8** is much higher than the corresponding sodium salts of the acids, which indicates that the carboxylate groups are monodentate under the conditions employed [36, 37]. This can be confirmed by X-ray crystal structure analyses of complexes **1**, **2**, **5** and **6**.

3.2.2. NMR spectra. The ^{1}H NMR spectra show the expected integrations and peak multiplicities. The single –OH resonance in the spectra of the free ligands is absent in the spectra of complexes **1–8** indicating the replacement of the carboxylic acid protons by a triorganotin moiety on complex formation. In addition, the resonance at 9.30 for **1** is attributed to the protons of co-crystallizing water. The resonances at 1.25–1.37 and 3.15–3.20 in all complexes are from N–CH$_2$CH$_3$.

The ^{13}C 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 electron density transfer from the ligand to the metal. The single resonances at 170.75–173.65 are attributed to the COO group. These data are consistent with chain structures for **1–8**.

The ^{119}Sn NMR spectra of complexes **1–8** show resonances at –93 to –110 ppm. As reported in the literature [38], values of δ (^{119}Sn) 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 conclude that complexes **1–8** are all five-coordinate and this is confirmed by the X-ray crystal structures of complexes **1**, **2**, **5** and **6**.

3.3. *Molecule structure*

3.3.1. Structures of [(C$_2$H$_5$)$_3$NH][Me$_3$Sn(3,5-pdc)]·mH$_2$O (1) and [(C$_2$H$_5$)$_3$NH][Ph$_3$Sn(3,5-pdc)] (2). The crystal structure and the unit cell of **1** are illustrated in figures 1 and 2 respectively, and selected bond lengths and bond angles in table 2.

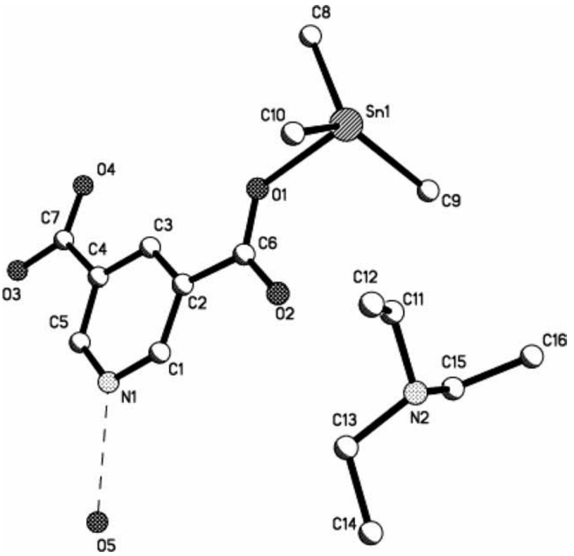


Figure 1. Atom labeling of complex **1**.

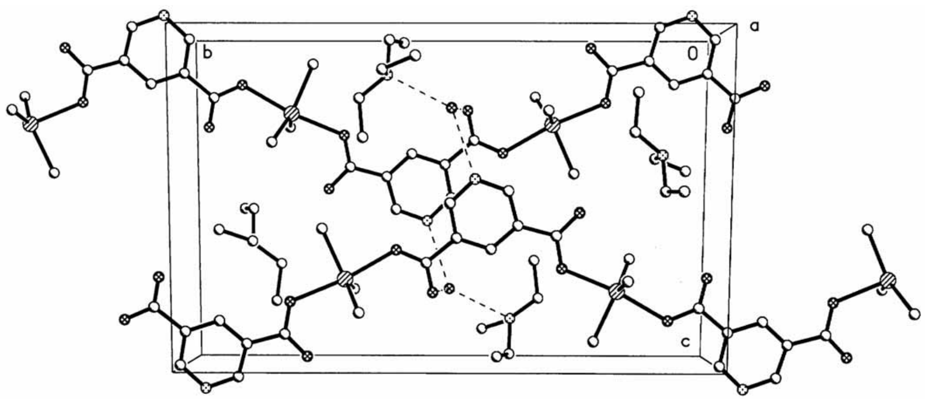


Figure 2. The unit cell of complex **1**.

As can be seen from figure 2, the crystal structure of **1** is polymeric in the solid state became bridging 3,5-pyridinedicarboxylate dianions. Each dianion bridges two Sn centers via one O atom of each carboxylate and the resulting polymer is aligned along the crystallographic *c*-axis. As a result of the bidentate mode of coordination of the dicarboxylic acid, each Sn center is five-coordinate and exists in a trigonal bipyramidal geometry with the O atoms occupying the axial sites [Sn(1)–O(1) 2.250(3) Å, Sn(1)–O(3)#1 2.251(3) Å and O(1)–Sn(1)–O(3)#1 172.13(12)°]. Significantly, the pyridine N atom does not participate in coordination to Sn. 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 associated with the non-coordinating O atoms are significantly shorter than the other two C–O bond distances.

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

Sn(1)–C(10)	2.113(5)	N(2)–C(11)	1.480(6)
Sn(1)–C(9)	2.114(5)	N(2)–C(15)	1.488(7)
Sn(1)–C(8)	2.120(4)	N(2)–C(13)	1.498(6)
Sn(1)–O(1)	2.250(3)	O(1)–C(6)	1.285(6)
Sn(1)–O(3)#1	2.251(3)	O(2)–C(6)	1.227(5)
N(1)–C(1)	1.334(5)	O(3)–C(7)	1.265(5)
N(1)–C(5)	1.339(6)	O(5)–H ··· O(4)#1	2.763
C(10)–Sn(1)–C(9)	127.3(2)	O(3)–C(7)–C(4)	114.4(4)
C(10)–Sn(1)–C(8)	113.8(2)	C(7)–O(3)–Sn(1)#2	126.3(3)
C(9)–Sn(1)–C(8)	118.8(2)	C(3)–C(2)–C(6)	122.6(4)
C(10)–Sn(1)–O(1)	91.40(2)	C(5)–C(4)–C(7)	120.4(4)
C(9)–Sn(1)–O(1)	93.53(2)	C(3)–C(4)–C(7)	121.6(4)
C(8)–Sn(1)–O(1)	87.65(2)	O(2)–C(6)–O(1)	125.7(4)
C(10)–Sn(1)–O(3)#1	93.08(2)	O(6)–C(6)–C(2)	119.5(4)
C(9)–Sn(1)–O(3)#1	88.90(2)	O(1)–C(6)–C(2)	114.7(4)
C(8)–Sn(1)–O(3)#1	84.62(2)	O(4)–C(7)–O(3)	126.2(4)
O(1)–Sn(1)–O(3)#1	172.13(1)	O(4)–C(7)–C(4)	119.4(4)
C(1)–N(1)–C(5)	116.1(4)	N(1)–O(5)–O(4)#1	95.11
C(11)–N(2)–C(15)	110.8(4)	N(2)–C(11)–C(12)	113.9(4)
C(11)–N(2)–C(13)	111.5(4)	N(2)–C(13)–C(14)	112.7(5)
C(6)–O(1)–Sn(1)	121.7(3)	C(16)–C(15)–N(2)	112.9(5)

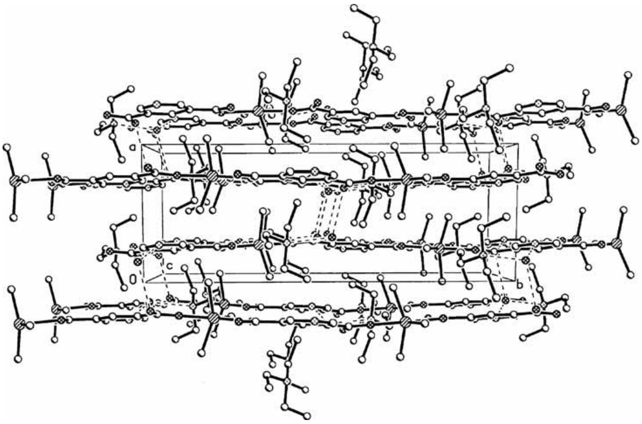


Figure 3. Perspective view showing the 2D network of **1**.

The intramolecular Sn(1) ··· O(2) and Sn(1) ··· O(4)#1 separations of 3.314 and 3.431 Å, respectively do not indicate bonding interactions between these atoms. Although not involved in coordination to Sn, the O(2) and O(4)#1 atoms form significant intermolecular contacts in the crystal lattice.

Hydrogen bond interactions are usually important in supramolecular architecture. In **1** between adjacent [$(C_2H_5)_3NH$][Me_3Sn(3,5-pdc)] polymeric chains there exists a co-crystallized water molecule with distances of O(5)–H ··· N(1) and O(5)–H ··· O(4)#1 are 2.842 and 2.763 Å, respectively. The angle of N(1)–O(5)–O(4)#1 is 95.11°. In complex **1**, there exist triethylammonium cations, linked to water through hydrogen bonds with a distance of N–H ··· O of 2.760 Å and N–H–O angle of 177.32°. Such intermolecular hydrogen bonding interactions between layers result in a 2D network, shown in figure 3. The water molecules play an important role in stabilization of the layer structure and control of the orientation of the 3,5-H_2pdc ligand.

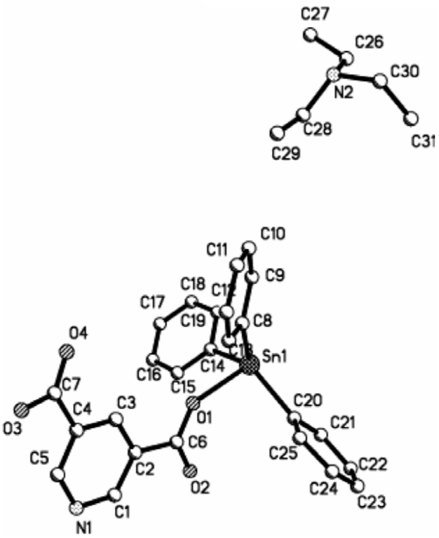


Figure 4. Atom labeling of complex **2**.

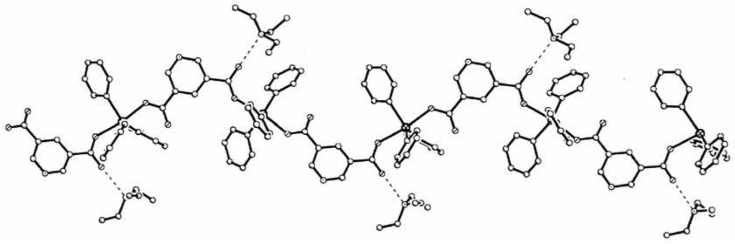


Figure 5. The 1D polymeric chain and mode of association between anions and cations in the lattice of **2**.

The X-ray diffraction investigation of complex **2** indicates two independent molecules in the unit cell, each associated in an infinite polymeric chain in the solid state owing to the presence of bridging 3,5-pyridinedicarboxylate dianions. The differences in the bond lengths and angles within the two molecules may arise from packing effects in the crystals. The molecular structure and polymeric chain of **2** are shown in figures 4 and 5. Selected bond lengths and angles are listed in table 2.

Similar to complex **1**, as shown in figure 5, each dianion bridges two Sn centers via only one O atom of each carboxylate moiety. As a result of the bidentate coordination of the dicarboxylic acid, each Sn center is five-coordinate and exists in trigonal bipyramidal geometry with O atoms occupying the axial sites [Sn(1)–O(1) 2.231(4), Sn(1)–O(3)#1 2.194(4) Å which are slightly shorter than in complex **1** and O(1)–Sn(1)–O(3)#1 171.14(14)° which is also slightly smaller than in **1** 172.13(12)°]. As expected the C–O bond distances associated with the non-coordinating O atoms are significantly shorter than the other two C–O bond distances. The intramolecular Sn(1) $\cdots$ O(2) and Sn(1) $\cdots$ O(4)#1 separations of 3.696 and 3.425 Å, respectively, indicate no bonding interactions these atoms. Although not involved in coordination to Sn, the O(2) and O(4)#1 atoms form significant intermolecular contacts in the crystal lattice.

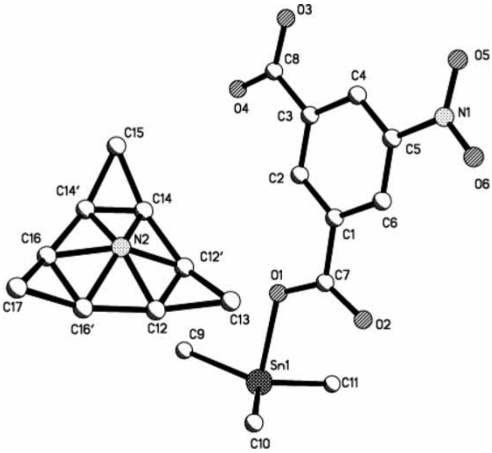


Figure 6. Atom labeling of complex **5**.

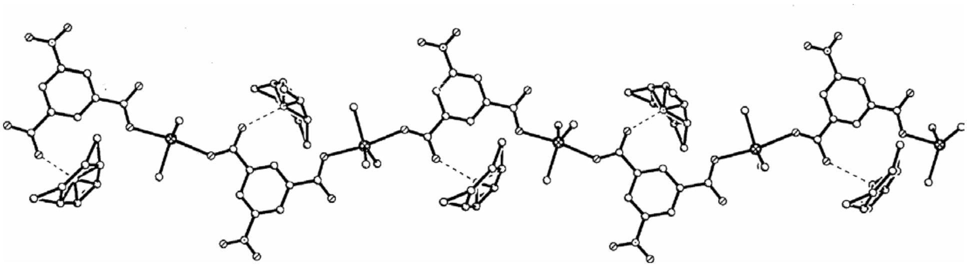


Figure 7. The 1D polymeric chain and mode of association between anions and cations in the lattice of **5**.

Associated with the polymeric chain, via hydrogen bonding contacts, are the triethylammonium cations as shown in figure 5. The ammonium bound H atoms hydrogen-bond to the pendant O atoms, O(2), such that the N(2)–H(2)$\cdots$O(2) is 2.777 Å, and the N(2)–H(2)–O(2) angle is 159.22°.

3.3.2. Structures of $[(C_2H_5)_3NH][Me_3Sn(5\text{-nip})]$ (5) and $[(C_2H_5)_3NH][Ph_3Sn(5\text{-nip})]$ (6). Complex **5** shows two independent molecules in the unit cell, associated in an infinite polymeric chain in the solid state by bridging through 5-nitroisophthalate dianions. Differences in the bond lengths and angles within the two molecules may result from packing effects in the crystals. The molecular structure, the unit cell and the polymeric chain of **5** are shown in figures 6, 7 and 8, respectively. Selected bond lengths and angles are listed in table 3.

As shown in figure 8, each dianion bridges two Sn centers via one O atom of each carboxylate. As a result of the bidentate coordination of the dicarboxylic acid, each Sn center is five-coordinate in a trigonal bipyramidal geometry with the O atoms occupying the axial sites [Sn(1)–O(1) 2.238(3), Sn(1)–O(3)#1 2.282(3) Å and O(1)–Sn(1)–O(3)#1 172.27(12)°]. The intramolecular Sn(1)$\cdots$O(2) and Sn(1)$\cdots$O(4)#1 separations of 3.258 and 3.795 Å, respectively are not indicative of bonding interactions between these atoms.

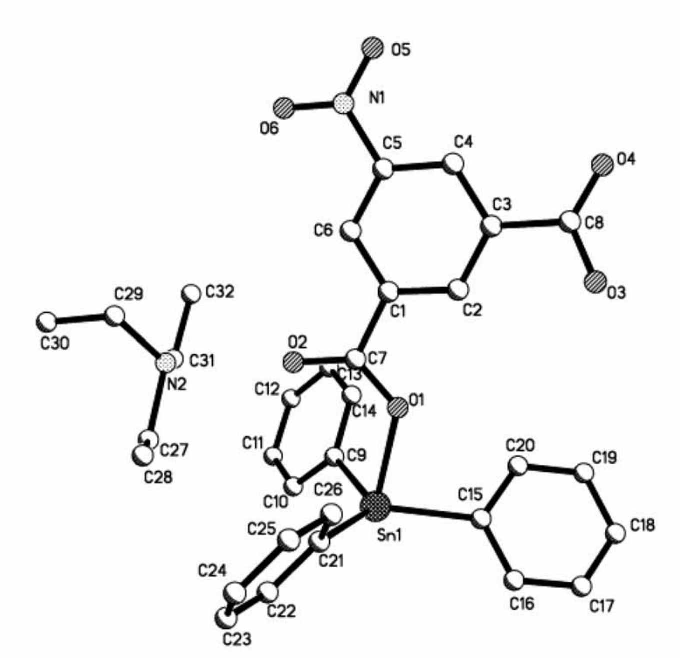


Figure 8. Atom labeling of complex **6**.

Table 3. Selected bond lengths (Å) and angles (°) for complex **2**.

Sn(1)–C(20)	2.130(6)	C(7)–O(3)	1.296(6)
Sn(1)–C(14)	2.138(7)	C(7)–O(4)	1.209(6)
Sn(1)–C(8)	2.146(5)	C(2)–C(6)	1.527(7)
Sn(1)–O(3)#1	2.194(4)	C(4)–C(7)	1.509(7)
Sn(1)–O(1)	2.231(4)	N(1)–C(1)	1.346(7)
C(6)–O(1)	1.264(7)	N(1)–C(5)	1.348(8)
C(6)–O(2)	1.231(7)		
C(20)–Sn(1)–C(14)	130.6(2)	C(5)–C(4)–C(7)	121.3(5)
C(1)–Sn(1)–C(8)	111.8(2)	C(3)–C(4)–C(7)	120.8(5)
C(14)–Sn(1)–C(8)	117.4(2)	O(2)–C(6)–O(1)	126.9(5)
C(20)–Sn(1)–O(3)#1	94.09(2)	O(2)–C(6)–C(2)	118.8(5)
C(14)–Sn(1)–O(3)#1	91.99(2)	O(1)–C(6)–C(2)	114.3(5)
C(8)–Sn(1)–O(3)#1	87.50(2)	O(4)–C(7)–O(3)	125.2(5)
C(20)–Sn(1)–O(1)	91.77(2)	O(4)–C(7)–C(4)	120.5(5)
C(14)–Sn(1)–O(1)	89.25(2)	O(3)–C(7)–C(4)	114.3(5)
C(8)–Sn(1)–O(1)	84.15(2)	C(13)–C(8)–Sn(1)	122.2(4)
O(3)#1–Sn(1)–O(1)	171.14(1)	C(9)–C(8)–Sn(1)	120.0(5)
C(6)–O(1)–Sn(1)	137.9(4)	C(15)–C(14)–Sn(1)	123.7(6)
C(7)–O(3)–Sn(1)#2	128.0(4)	C(19)–C(14)–Sn(1)	120.2(6)
C(1)–C(2)–C(6)	121.3(5)	C(25)–C(20)–Sn(1)	119.4(5)
C(3)–C(2)–C(6)	121.5(5)	C(21)–C(20)–Sn(1)	124.4(5)

Associated with the polymeric chain, via hydrogen bonding contacts, are the triethylammonium cations as shown in figure 8. The ammonium bound H atoms hydrogen bond to pendant O atoms, such that N(2)–H–O(4) is 2.780 Å.

The molecular structure and polymeric chain of **6** are shown in figures 9 and 10. Selected bond lengths and angles are listed in table 5. Similar to **5**, complex **6** is

Table 4. Selected bond lengths (Å) and angles (°) for complex **5**.

Sn(1)–C(10)	2.106(5)	O(2)–C(7)	1.225(6)
Sn(1)–C(11)	2.113(5)	O(3)–C(8)	1.261(5)
Sn(1)–C(9)	2.119(5)	O(4)–C(8)	1.240(6)
Sn(1)–O(1)	2.238(3)	C(1)–C(7)	1.511(6)
Sn(1)–O(3)#1	2.282(3)	C(3)–C(8)	1.515(6)
O(1)–C(7)	1.283(6)		
C(10)–Sn(1)–C(11)	127.3(2)	C(16′)–N(2)–C(16)	126.3(3)
C(10)–Sn(1)–C(9)	113.8(2)	C(14′)–N(2)–C(14)	122.6(4)
C(11)–Sn(1)–C(9)	118.8(2)	C(7)–O(1)–Sn(1)	120.4(4)
C(10)–Sn(1)–O(1)	91.40(2)	C(8)–O(3)–Sn(1)#2	121.6(4)
C(11)–Sn(1)–O(1)	93.53(2)	O(2)–C(7)–O(1)	125.7(4)
C(9)–Sn(1)–O(1)	87.65(2)	O(2)–C(7)–C(1)	119.5(4)
C(10)–Sn(1)–O(3)#1	93.08(2)	O(1)–C(7)–C(1)	114.7(4)
C(11)–Sn(1)–O(3)#1	88.90(2)	O(4)–C(8)–O(3)	126.2(4)
C(9)–Sn(1)–O(3)#1	84.62(2)	O(4)–C(8)–C(3)	119.4(4)
O(1)–Sn(1)–O(3)#1	172.13(1)	O(3)–C(8)–C(3)	114.4(4)
O(5)–N(1)–O(6)	116.1(4)	N(2)–C(14)–C(15)	112.9(6)
C(12)–N(2)–C(12′)	110.8(4)	N(2)–C(16)–C(17)	109.5(6)

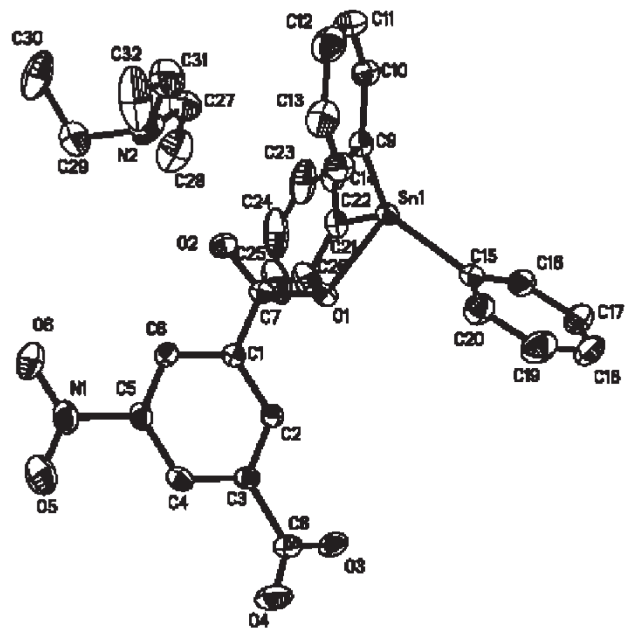


Figure 9. The 1D polymeric chain and mode of association between anions and cations in the lattice of **6**.

also an infinite polymeric chain in the solid state. As shown in figure 10, each dianion bridges two Sn centers via one O atom of each carboxylate moiety. As a result, each Sn center is five-coordinate and exists in trigonal bipyramidal geometry with the O atoms occupying the axial sites [Sn(1)–O(1) 2.2280(17), Sn(1)–O(3)#1 2.2918(18) Å and O(1)–Sn(1)–O(3)#1 175.24(7)° which is slightly larger than in **5** (172.27(12)°)].

For complex **6**, similar to complex **5**, the ammonium bound H atoms hydrogen bond to the pendant O atom O(2), such that the N(2)–H(2)···O(2) is 2.748 Å, and the N(2)–H(2)–O(2) angle is 162.43°.

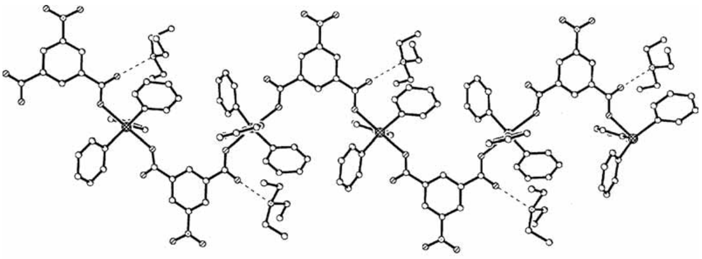


Figure 10. The 1D polymeric chain and mode of association between anions and cations in the lattice of **6**.

Table 5. Selected bond lengths (Å) and angles (°) for complex **6**.

Sn(1)–C(21)	2.124(3)	C(7)–O(2)	1.244(3)
Sn(1)–C(15)	2.139(3)	C(8)–O(3)	1.288(3)
Sn(1)–C(9)	2.146(3)	C(8)–O(4)	1.213(3)
Sn(1)–O(3)#1	2.2918(2)	C(1)–C(7)	1.508(3)
Sn(1)–O(1)	2.2280(2)	C(3)–C(8)	1.510(3)
C(7)–O(1)	1.275(3)	C(4)–C(5)	1.377(4)
C(21)–Sn(1)–C(15)	121.35(1)	C(8)–O(3)–Sn(1)#2	131.12(2)
C(21)–Sn(1)–C(9)	125.01(1)	C(2)–C(1)–C(7)	120.6(2)
C(15)–Sn(1)–C(9)	113.58(1)	C(4)–C(3)–C(8)	118.5(2)
C(21)–Sn(1)–O(3)#1	93.88(1)	C(2)–C(3)–C(8)	122.2(2)
C(15)–Sn(1)–O(3)#1	93.07(9)	C(6)–C(5)–N(1)	118.8(2)
C(9)–Sn(1)–O(3)#1	85.28(9)	C(4)–C(5)–N(1)	117.7(2)
C(21)–Sn(1)–O(1)	90.44(1)	O(2)–C(7)–O(1)	126.4(2)
C(15)–Sn(1)–O(1)	86.37(9)	O(2)–C(7)–C(2)	119.5(2)
C(9)–Sn(1)–O(1)	90.61(9)	O(1)–C(7)–C(1)	114.2(2)
O(1)–Sn(1)–O(3)#1	175.24(7)	O(4)–C(8)–O(3)	127.0(3)
C(7)–O(1)–Sn(1)	127.26(2)	O(4)–C(8)–C(3)	119.5 (2)
O(3)–C(8)–C(3)	113.5(2)	C(10)–C(9)–Sn(1)	121.8(2)

In summary, through the reaction of triorganotin and dicarboxylic acids by adding triethylamine we obtained a series of ionic infinite polymeric chains. In complex **1**, the adjacent layers were linked by hydrogen bonds through co-crystallized water and a network was formed. We can see from the crystal structure of **1** that the water molecules in the polymers play an important role in the stabilization of the layer structure and the control of the orientation of the dicarboxylic acid ligands.

Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis of complexes **1**, **2**, **5** and **6** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 269143 **1**, 269142 **2**, 269144 **5** and 269146 **6**. 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; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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