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Syntheses and Crystal Structures of Triorganotin (IV) Derivatives with 2,2′-Bipyridine-4,4′-Dicarboxylic Acid

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ABSTRACT: *Four organotin complexes with 2,2′-bipyridine-4,4′-dicarboxylic acid, H_2dcbp: $(Ph_3Sn)_2(dcbp)$* **1**, *$[(PhCH_2)_3Sn]_2(dcbp)\cdot 2CH_3OH$* **2**, *$[(Me_3Sn)_2(dcbp)]_n$* **3**, *$[(Bu_3Sn)_2(dcbp)]_n$* **4** *have been synthesized. The complexes* **1–4** *were characterized by elemental, IR, ^1H,^{13}C,^{119}Sn NMR, and X-ray crystallographic analyses. Crystal structures show that complex* **1** *is a monomer with one ligand coordinated to two triorganotin moieties, and a 1D infinite polymeric chain generates via intermolecular C—H···N hydrogen bond; complex* **2** *is also a monomer and forms a 2D network by intermolecular O–H···O weak interaction; both of complexes* **3** *and* **4** *form 2D network structures where 2,2′–bipyridine-4,4′-dicarboxylate acts as a tetradentate ligand coordinated to trimethyltin and tri-n-butyltin ions, respectively.*

INTRODUCTION

Organotin carboxylates have received considerable attention because of their various structural types that may be adopted in the solid state. Several products such as monomers, dimers, tetramers, oligomeric ladders, and hexameric drums have been isolated [1–4]. It has also been demonstrated that other structural types are formed because of the presence of additional coordinating sites (e.g., N, O, S) along with a carboxylate moiety [5–6]. Chandrasekhar and coworkers have reported the self-assembly of macrocycle networks in the reaction of pyrazole-3,5-dicarboxylic acid and Bz_2SnCl_2 [7], García-Zarracino and Höpfl obtained the supramolecular architectures by the reaction of 2,5-pyridinodicarboxylic acid and R_2SnO (R = Me, *n*-Bu, Ph) [8]. Wang reported a monomer with 2,2′-biquinoline-4,4′-dicarboxylate and triphenyltin chloride [9]. In our previous work, we have also reported several novel molecular structures on it, such as two 15-membered trinuclear macrocyclic complexes with 2-pyrazinecarboxylic acid [10], and a series of triorganotin pyridinedicarboxylates with 2,5-, 3,5-, and 2,6-pyridinedicarboxylic acid [11]. To continue our research, we selected another interesting ligand, 2,2′-bipyridine-4,4′-dicarboxylic acid, on the basis of the following considerations: (a) the 2,2′-bipyridine and carboxylate functional groups of H_2dcbp all have coordinate abilities, either singly or in unison, so several potential multiple molecular models in organotin complexes may be possess; (b) it can act not only as a hydrogen bond acceptor but also as a hydrogen bond donor, so the preparation of hybrid networks combining the strength of coordination bonding with the flexibility of hydrogen bonding is also feasible; and (c) it possesses high symmetry that

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may be helpful for the crystal growth of the product formed.

The synthesis and characterization of some transition metal complexes of 2,2′-bipyridine-4,4′-dicarboxylic acid have been carried out previously [12–19]. Besides, the preparation and the crystal of structures of trimethyltin derivative of 2,2′-bipyridine-4,4′-dicarboxylic acid have been reported by Stocco et al. [20]. They obtained the complex by the condensation of H_2dcbp and Me_3SnOH in 1:2 molar ratio, but we employ Me_3SnCl instead of Me_3SnOH to prepare the complex. Herein, we report four triorganotin (IV) complexes constructed from H_2dcbp, with a 1:2:2 molar ratio of H_2dcbp: EtONa: R_3SnCl.

EXPERIMENTAL DETAILS

Materials and Measurements

Trimethyltin chloride, triphenyltin chloride, tri-*n*-butyltin chloride and 2,2′-bipyridine-4,4′-dicarboxylic acid and were commercially available, and they were used without purification. Tribenzyltin (IV) chloride was prepared by a standard method reported in the literature [21]. The melting points were obtained with Kofler micro melting point apparatus and uncorrected. Infrared spectra were recorded on a Nicolet-5700 (Thermo Electron Corporation) spectrophotometer using KBr disks and sodium chloride optics. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on Varian Mercury Plus400 (Varian Medical Systems) 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 parts per million (ppm) with respect to the references and are stated relative to external tetramethylsilane for ^{1}H and ^{13}C NMR and Me_4Sn for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400II apparatus.

Syntheses of the Complexes **1–4**

$(Ph_3Sn)_2$(dcbp) **1**. The reaction is carried out under nitrogen atmosphere. The 2,2′-bipyridine-4,4′-dicarboxylic acid (0.244 g, 1 mmol) and the sodium ethoxide (0.136 g, 2 mmol) were added to the solution of methanol (30 mL) in a Schlenk flask and stirred for 30 min. Then the triphenyltin chloride (0.771 g, 2 mmol) was added to the reactor, the reaction mixture was stirred for 12 h at 40°C. After cooling down to room temperature, it was filtered. The solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was recrystallized from ether, and a transparent colorless crystal was formed. Yield: 85%; mp > 220°C. Anal. Calcd for $C_{48}H_{36}N_2O_4Sn_2$: C, 61.19; H, 3.85; N, 2.97%. Found: C, 60.93; H, 4.01; N, 2.71%. IR (KBr, cm^{-1}): ν_{as}(COO), 1635; ν_s(COO), 1331; ν(Sn–C), 558; ν(Sn–O), 447. ^{1}H NMR [$(CD_3)_2SO$, ppm]: $\delta = 7.59$–8.68 (m, 6H, bipyridine); 7.28–7.49 (m, 30H, Ph). ^{13}C NMR [$(CD_3)_2SO$, ppm]: $\delta = 170.16$ (COO); 121.85, 124.06, 142.25, 150.77, 157.11 [bipyridine(=CH)]; 130.43–137.43 (Ar–C). ^{119}Sn NMR [$(CD_3)_2SO$, ppm]: −44.8.

$[(PhCH_2)_3Sn]_2(dcbp)\cdot 2CH_3OH$ **2**. The procedure is similar to that of complex **1**: 2,2′-bipyridine-4,4′-dicarboxylic acid (0.244 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol), and tribenzyltin chloride (0.854 g, 2 mmol) were reacted for 12 h at 40°C. Recrystallized from methanol, a transparent colorless crystal was formed. Yield: 78%; mp > 220°C. Anal. Calcd for $C_{56}H_{56}N_2O_6Sn_2$: C, 61.18; H, 5.18; N, 2.57%. Found: C, 60.98; H, 5.37; N, 2.31%. IR (KBr, cm^{-1}): ν(OH), 3207; ν_{as}(COO), 1636; ν_s(COO), 1337; ν(Sn—C), 560; ν(Sn—O), 452.^{1}H NMR [$(CD_3)_2SO$, ppm]: $\delta = 7.56$–8.70 (m, 6H, bipyridine); 6.96–7.31 (m, 30H, Ph), 2.63 (s, 12H, Ph—CH_2), 4.54 (s, 2H, O—H), 3.31 (s, 6H, O—CH_3), ^{13}C NMR[$(CD_3)_2SO$, ppm]: $\delta = 170.08$ (COO); 120.09, 122.56, 139.39, 149.34, 155.67 [bipyridine(=CH)]; 130.43–137.43 (Ar—C); 26.63 (Ph—CH_2). ^{119}Sn NMR [$(CD_3)_2SO$, ppm]: −152.7.

$[(Me_3Sn)_2(dcbp)]_n$ **3**. The procedure is similar to that of complex **1**,2,2′-bipyridine-4,4′-dicarboxylic acid (0.244 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and trimethyltin chloride (0.398 g, 2 mmol) were reacted for 12 h at 40°C. Recrystallized from ether, a transparent colorless crystal was formed. Yield: 81%; mp > 220°C. Anal. Calcd for $C_{18}H_{24}N_2O_4Sn_2$: C, 37.94; H, 4.25; N, 4.92%. Found: C, 37.61; H, 4.57; N, 4.70%. ν_{as}(COO), 1614; ν_s(COO), 1403; ν(Sn—C), 550; ν(Sn—O), 476. ^{1}H NMR [$(CD_3)_2SO$, ppm]: $\delta = 7.32$–8.77 (m, 6H, bipyridine); 0.85–0.88 (s, 18H, CH_3). ^{13}C NMR[$(CD_3)_2SO$, ppm]: $\delta = 169.38$ (COO); 120.09, 122.56, 139.39, 149.34, 155.67 [bipyridine(=CH)]; 14.56 (CH_3). ^{119}Sn NMR [$(CD_3)_2SO$, ppm]: −127.4.

$[(Bu_3Sn)_2(dcbp)]_n$ **4**. The procedure is similar to that of complex **1**,2,2′-bipyridine-4,4′-dicarboxylic acid (0.244 g, 1 mmol), sodium ethoxide (0.136 g, 2 mmol) and tri-*n*-butyltin chloride (0.651 g, 2 mmol) were reacted for 12 h at 40°C. Recrystallized from ether-petroleum, a transparent colorless crystal was formed. Yield: 88%; mp >220°C. Anal. Calcd for $C_{72}H_{120}N_4O_8Sn_4$: C, 52.58, H, 7.35; N,

3.41%. Found: C, 52.42; H, 7.51; N, 3.24%. ν_{as}(COO), 1613; ν_s(COO), 1403; ν(Sn—C), 524; ν(Sn—O), 471. ^{1}H NMR [$(CD_3)_2SO$, ppm]: $\delta = 7.27$–8.81 (m, 12H, bipyridine); 1.34–1.73 (m, 72H, $CH_2CH_2CH_2$); 0.91–0.95 (t, 36H, CH_3). ^{13}C NMR [$(CD_3)_2SO$, ppm]: δ 170.04 (COO); 121.59, 123.89, 141.09, 150.04, 156.97 [bipyridine(=CH)); 13.83, 26.02, 27.25, 28.13 (*n*-Bu). ^{119}Sn NMR [$(CD_3)_2SO$, ppm]: −105.9.

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 MoKα 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 SHELXS-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

RESULT AND DISCUSSION

Syntheses of the Complexes **1–4**

The syntheses procedures are shown in Scheme 1.

IR Spectroscopic Studies of the Complexes **1–4**

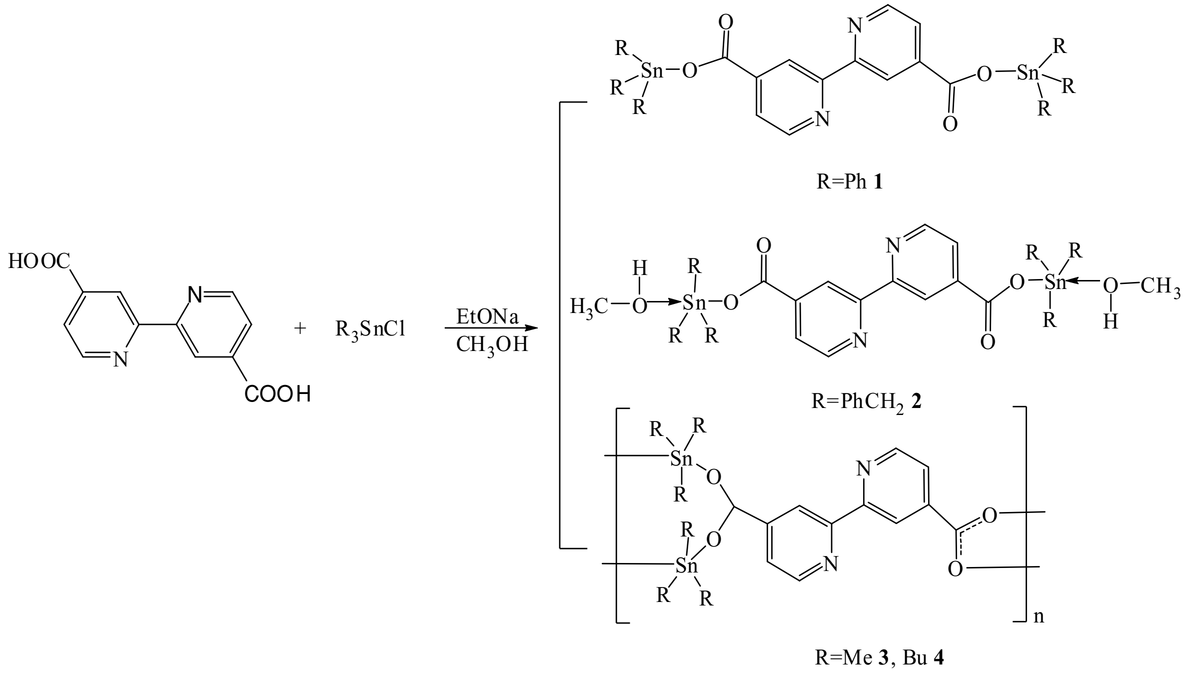
The stretching frequencies of interest are those associated with the C(O)O, Sn—C, and Sn—O groups. The strong absorption in the region 447–476 cm^{-1}, which is absent in the spectrum of the free ligand, is assigned to the Sn—O stretching mode. All these values are consistent with those detected in a number of organotin (IV)-oxygen derivatives [22,23]. Comparing the IR spectra of the free ligand with complexes **1, 3**, and **4**, the explicit feature is the absence of a band in the region 3200–3500 cm^{-1}, which appears in the free ligand as the —OH stretching vibration, thus indicating metal-ligand bond formation through this site. The IR spectrum of **2** exhibits a broad band at 3207 cm^{-1}, attributed to ν(MeO—H) stretching vibration.

^{1}H NMR, ^{13}C NMR, and ^{119}Sn NMR Data of Complexes **1–4**

The ^{1}H NMR spectra show the expected integration and peak multiplicities. The single resonance of —OH in the spectra of the free ligand is absent in the spectra of all the complexes**1–4** indicating the replacement of the carboxylic acid protons by a triorganotin moiety on complex formation.

TABLE 1 Crystal Data and Refinement Details for Complexes **1, 2**, and **4**

Complex	**1**	**2**	**4**
Empirical formula	$C_{48}H_{36}N_2O_4Sn_2$	$C_{56}H_{56}N_2O_6Sn_2$	$C_{72}H_{120}N_4O_8Sn_4$
Formula weight	942.17	1,090.41	1,644.48
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2(1)/*c*	P-1
a (Å)	13.1560(13)	9.1017(10)	20.563(2)
b (Å)	14.9691(18)	12.7688(12)	20.569(2)
c (Å)	17.420(3)	22.927(3)	25.012(3)
α(°)	72.171(2)	90	110.077(2)
β(°)	81.329(3)	101.246(2)	93.9170(10)
γ(°)	69.270(2)	90	90.0460(10)
V(Å^3)	3,051.0(6)	2,613.4(5)	9,910.0(19)
Z	3	2	4
D_{calc}	1.538	1.386	1.102
F(000)	1,410	1,108	3,376
μ (mm^{-1})	1.275	1.005	1.037
Crystal size	0.24 × 0.18 × 0.13	0.50 × 0.49 × 0.27	0.50 × 0.40 × 0.20
θ Range (°)	1.23–25.01	1.81–25.00	1.2–25.01
Reflection collected	15,652	12,518	50,572
Independent reflections	10,539	4,473	33,969
Data/restraints/parameters	10,539/0/757	4,473/486/ 99	33,969/3,635/1,607
Goodness-of-fit on	1.068	1.005	1.030
Final *R* indices [$I > 2$ sigma (I)]	$R_1 = 0.0520$ $wR_2 = 0.1050$	$R_1 = 0.0556$ $wR_2 = 0.1173$	$R_1 = 0.0762$ $wR_2 = 0.1552$
R indices (all data)	$R_1 = 0.1202$ $wR_2 = 0.1371$	$R_1 = 0.0694$ $wR_2 = 0.1270$	$R_1 = 0.1992$ $wR_2 = 0.1685$



SCHEME 1

The ^{13}C NMR spectra of all complexes show a significant downfield shift of all carbon resonances compared with the free ligands; the shift is a consequence of an electron density transfer from the ligand to the metal atoms. The single resonances at 169.38–170.16 are attributed to the COO$^-$ groups in the complexes **1–4**. These data are consistent with the structures of **1–4**.

The ^{119}Sn NMR spectra of complexes **1–4** show resonances between −44.8 and −152.7 ppm. As reported in the literature [24], we can conclude that complex **1** ($\delta = -44.8$) is typical of four-coordinate and complexes **2–4** ($\delta = -152.7$, -127.4, -105.9) are typical five-coordinate. This is confirmed by the X-ray crystal structures.

Crystal Structures of Complexes 1*,* 2*, and* 4

Structures of Complexes **1** *and* **2**. The crystal structures of complexes **1** and **2** are shown in Figs. 1

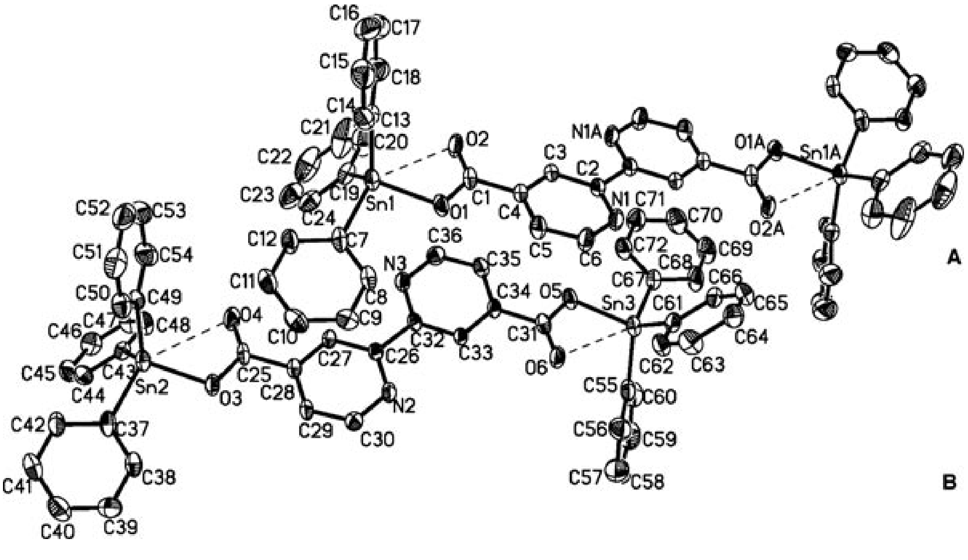


FIGURE 1 The molecular structure of complex **1**.

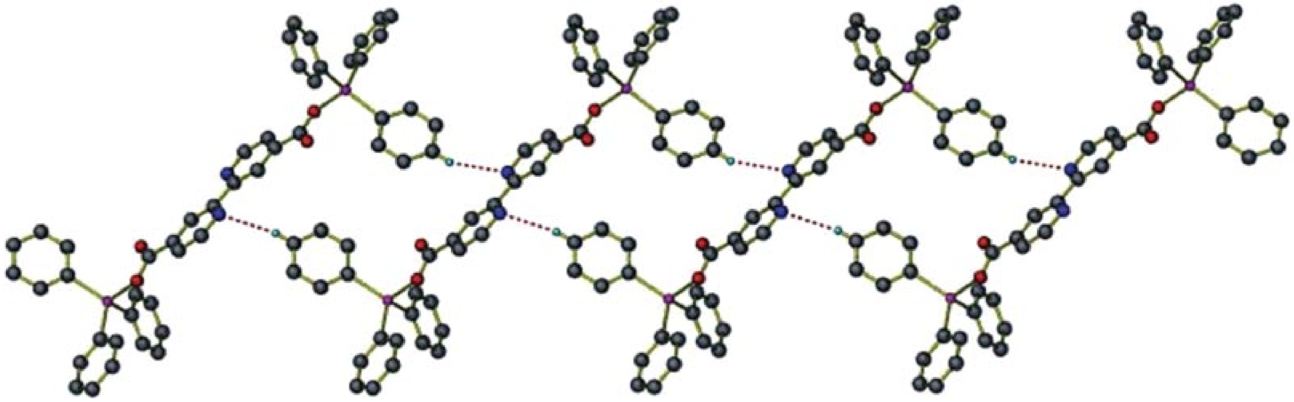


FIGURE 2 The 1D infinite chain structure of complex connected by intermolecular C—H···N hydrogen bonding.

and 2, and selected bond lengths and angles are given in Tables 2 and 3, respectively.

For complex **1**, the asymmetric unit contains two monomers A and B, which are crystallographically nonequivalent. The conformations of the two independent molecules A and B are almost the same, with only small differences in bond lengths and bond angles. Each discrete molecule is a monomer with one ligand coordinated to two triorganotin moieties. As follows, the Sn(1)–O(1) [2.054(5) Å] bond length lies

TABLE 2 Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Bond lengths			
Sn(1)–O(1)	2.054(5)	Sn(2)–C(43)	2.128(8)
Sn(1)–C(13)	2.112(9)	Sn(2)–C(37)	2.129(9)
Sn(1)–C(19)	2.115(9)	Sn(3)–O(5)	2.049(5)
Sn(1)–C(7)	2.128(8)	Sn(3)–C(67)	2.102(8)
Sn(2)–O(3)	2.050(5)	Sn(3)–C(55)	2.118(9)
Sn(2)–C(49)	2.122(8)	Sn(3)–C(61)	2.126(8)
Bond angles			
O(1)–Sn(1)–C(13)	104.7(3)	O(3)–Sn(2)–C(37)	95.7(3)
O(1)–Sn(1)–C(19)	115.2(3)	C(49)–Sn(2)–C(37)	111.1(3)
C(13)–Sn(1)–C(19)	116.3(4)	C(43)–Sn(2)–C(37)	111.2(3)
O(1)–Sn(1)–C(7)	94.6(3)	O(5)–Sn(3)–C(55)	108.8(3)
C(13)–Sn(1)–C(7)	111.8(3)	C(67)–Sn(3)–C(55)	110.1(4)
C(19)–Sn(1)–C(7)	112.0(3)	O(5)–Sn(3)–C(61)	111.9(3)
O(3)-Sn(2)–C(49)	105.8(3)	C(67)–Sn(3)–C(61)	113.6(3)
O(3)–Sn(2)–C(43)	114.1(3)	C(55)–Sn(3)–C(61)	116.2(3)
C(49)–Sn(2)–C(43))	116.9(3)		

TABLE 3 Selected Bond Lengths (Å) and Bond Angles (°) for **2**

Bond lengths			
Sn(1)–C(21)	2.124(6)	Sn(1)–C(14)	2.139(7)
Sn(1)–O(1)	2.123(4)	Sn(1)–O(3)	2.497(5)
Bond angles			
C(21)–Sn(1)–O(1)	93.7(2)	C(14)–Sn(1)–C(7)	120.5(3)
C(21)–Sn(1)–C(14)	117.2(3)	C(21)–Sn(1)–O(3)	77.4(2)
O(1)–Sn(1)–C(14)	100.5(2)	O(1)–Sn(1)–O(3)	170.25(17)
C(21)–Sn(1)–C(7)	118.4(3)	C(14)–Sn(1)–O(3)	87.2(2)
O(1)–Sn(1)–C(7)	95.6(3)	C(7)–Sn(1)–O(3)	85.3(3)
C(1)–O(1)–Sn(1)	123.7(4)		

Symmetry code: #1 $-x+1$, $-y$, $-z+1$.

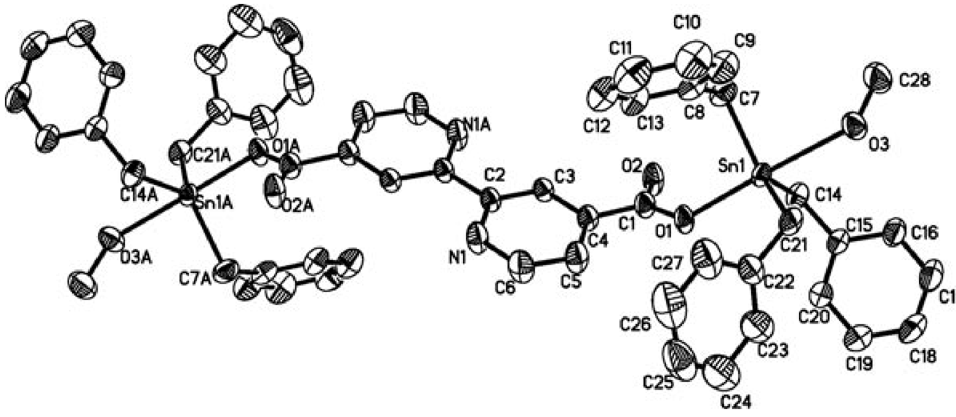


FIGURE 3 The molecular structure of complex **2**.

in the range that has been reported as the Sn—O covalent bond length [2.054(3)–2.083 Å] [25]; the Sn(2)–O(3) [2.050(5) Å] and the Sn(3)–O(5) [2.049(5) Å] are little shorter than the reported. All the Sn—O bond lengths are shorter than the sum of the covalent radii of Sn and O (2.13 Å) [26] so they all prove that the oxygen atoms are coordinated to the tin atoms by a strong chemical bond.

Furthermore, it is noteworthy that a weak intramolecular Sn···O interaction is recognized between the Sn(1) and O(2), Sn(2) and O(4), and Sn(3) and O(6). Although the distances of Sn(1)···O(2) [2.815 Å], Sn(2)···O(4) [2.878 Å], and Sn(3)···O(6) [2.853 Å] are all considerably longer than the normal Sn—O covalent bond length, they lie in the range of Sn···O distances of (2.61–3.02 Å), which have been confidently reported for intramolecular bonds [27,28]. As the oxygen atom is involved in a weak coordinative interaction with tin along one of the tetrahedral faces, the structure distortion for the tin atom in complex **1** is best described as a capped tetrahedral.

Moreover, intermolecular C—H···N hydrogen bonds are recognized in complex **1**, which linked

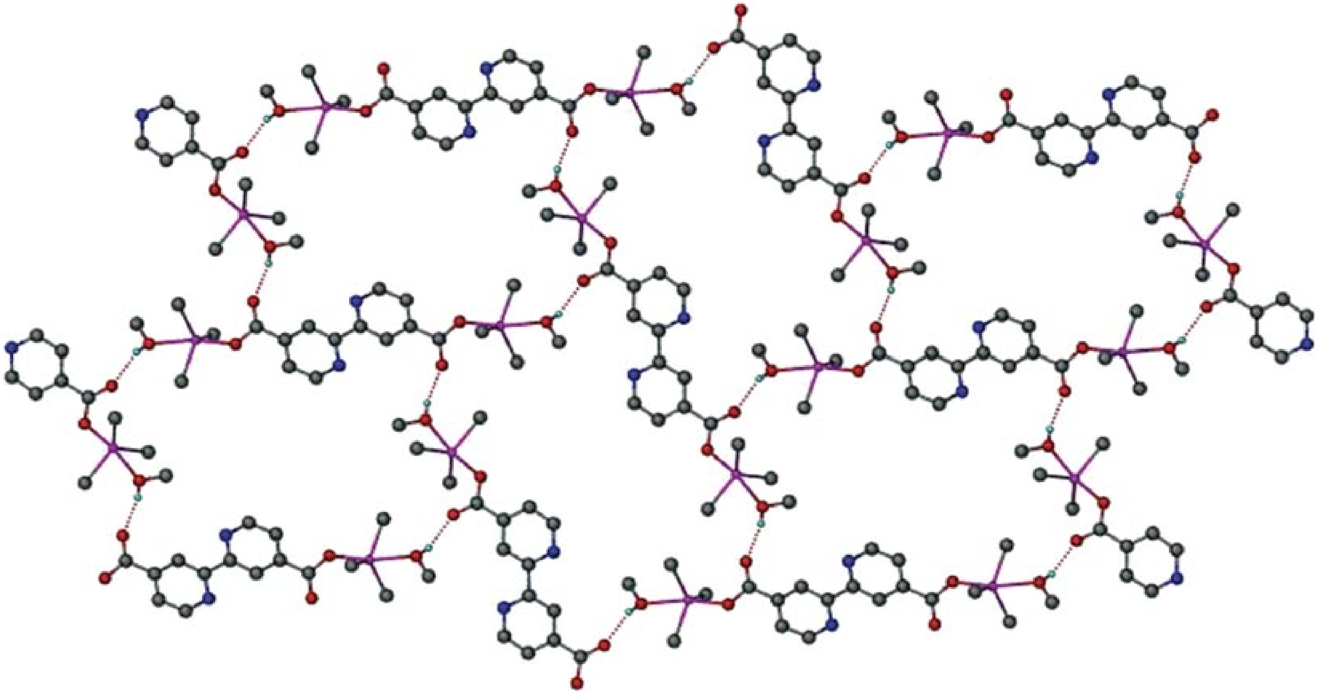


FIGURE 4 The 2D network structure of complex **2** connected by intermolecular O—H···O hydrogen bonding.

TABLE 4 Selected Bond Lengths (Å) and Bond Angles (°) for **4**

Bond lengths			
Sn(1)–C(33)	2.120(14)	Sn(5)–C(101)	2.154(13)
Sn(1)–C(29)	2.136(12)	Sn(5)–C(105)	2.181(12)
Sn(1)–C(25)	2.136(13)	Sn(5)–O(9)	2.168(8)
Sn(1)–O(1)	2.161(7)	Sn(5)–O(16)	2.591(11)
Sn(1)–O(8)	2.575(11)	Sn(6)–C(117)	2.101(11)
Sn(2)–C(45)	2.102(14)	Sn(6)–C(113)	2.140(12)
Sn(2)–C(37)	2.116(13)	Sn(6)–C(109)	2.162(12)
Sn(2)–C(41)	2.150(12)	Sn(6)–O(11)	2.168(8)
Sn(2)–O(3)	2.149(8)	Sn(6)–O(14)	2.594(11)
Sn(3)–C(57)	2.107(13)	Sn(7)–C(125)	2.106(13)
Sn(3)–C(53)	2.145(13)	Sn(7)–C(121)	2.127(14)
Sn(3)–C(49)	2.170(13)	Sn(7)–O(13)	2.149(8)
Sn(3)–O(5)	2.163(8)	Sn(7)–C(129)	2.156(13)
Sn(3)–O(2)	2.594(11)	Sn(7)–O(10)	2.577(11)
Sn(4)–C(65)	2.157(8)	Sn(8)–C(133)	2.103(14)
Sn(4)–C(69)	2.161(12)	Sn(8)–C(141)	2.095(13)
Sn(4)–O(7)	2.157(8)	Sn(8)–C(137)	2.139(13)
Sn(4)–C(61)	2.174(14)	Sn(8)–O(15)	2.152(7)
Sn(5)–C(97)	2.119(12)		
Bond angles			
C(33)–Sn(1)–C(29)	120.4(5)	C(101)–Sn(5)–C(105)	124.5(5)
C(33)–Sn(1)–C(25)	123.7(6)	C(97)–Sn(5)–O(9)	92.1(4)
C(29)–Sn(1)–C(25)	112.8(6)	C(101)–Sn(5)–O(9)	99.1(4)
C(33)–Sn(1)–O(1)	98.6(4)	C(105)–Sn(5)–O(9)	96.4(4)
C(29)–Sn(1)–O(1)	91.4(4)	C(97)–Sn(5)–O(16)	81.8(4)
C(25)–Sn(1)–O(1)	97.0(4)	C(101)–Sn(5)–O(16)	80.7(4)
C(33)–Sn(1)–O(8)	80.8(4)	C(105)–Sn(5)–O(16)	89.6(4)
C(29)–Sn(1)–O(8)	81.6(4)	O(9)–Sn(5)–O(16)	172.7(3)
C(25)–Sn(1)–O(8)	90.4(4)	C(117)–Sn(6)–C(113)	121.5(5)
O(1)–Sn(1)–O(8)	171.3(3)	C(117)–Sn(6)–C(109)	113.7(5)
C(45)–Sn(2)–C(37)	124.8(6)	C(113)–Sn(6)–C(109)	121.5(5)
C(45)–Sn(2)–C(41)	119.0(6)	C(117)–Sn(6)–O(11)	95.0(4)
C(37)–Sn(2)–C(41)	113.3(6)	C(113)–Sn(6)–O(11)	100.9(4)
C(45)–Sn(2)–O(3)	98.3(4)	C(109)–Sn(6)–O(11)	92.1(4)
C(37)–Sn(2)–O(3)	96.4(4)	C(117)–Sn(6)–O(14)	91.5(4)
C(41)–Sn(2)–O(3)	91.7(4)	C(113)–Sn(6)–O(14)	79.2(4)
C(57)–Sn(3)–C(53)	114.0(6)	C(109)–Sn(6)–O(14)	81.4(4)
C(57)–Sn(3)–C(49)	123.7(5)	O(11)–Sn(6)–O(14)	172.3(3)
C(53)–Sn(3)–C(49)	119.9(6)	C(125)–Sn(7)–C(121)	121.2(5)
C(57)–Sn(3)–O(5)	95.3(5)	C(125)–Sn(7)–O(13)	91.4(4)
C(53)–Sn(3)–O(5)	91.0(4)	C(121)–Sn(7)–O(13)	98.6(4)
C(49)–Sn(3)–O(5)	98.4(4)	C(125)–Sn(7)–C(129)	112.5(6)
C(57)–Sn(3)–O(2)	90.7(4)	C(121)–Sn(7)–C(129)	123.3(5)
C(53)–Sn(3)–O(2)	82.1(4)	O(13)–Sn(7)–C(129)	96.8(4)
C(49)–Sn(3)–O(2)	82.2(4)	C(125)–Sn(7)–O(10)	81.4(4)
O(5)–Sn(3)–O(2)	172.3(3)	C(121)–Sn(7)–O(10)	81.1(4)
C(65)–Sn(4)–C(69)	113.0(6)	O(13)–Sn(7)–O(10)	171.2(3)
C(65)–Sn(4)–O(7)	90.8(5)	C(129)–Sn(7)–O(10)	90.7(4)
C(69)–Sn(4)–O(7)	96.5(4)	C(133)–Sn(8)–C(141)	118.9(5)
C(65)–Sn(4)–C(61)	120.2(6)	C(133)–Sn(8)–C(137)	124.2(5)
C(69)–Sn(4)–C(61)	124.2(5)	C(141)–Sn(8)–C(137)	114.1(6)
O(7)–Sn(4)–C(61)	98.5(4)	C(133)–Sn(8)–O(15)	96.8(4)
C(97)–Sn(5)–C(101)	120.2(6)	C(141)–Sn(8)–O(15)	92.7(4)
C(97)–Sn(5)–C(105)	112.5(5)	C(137)–Sn(8)–O(15)	96.8(4)

the molecular into a 1D linear chain. The distances [C—H···N (2.612 Å), C···N (3.476 Å)], and the angle [C—H···N (154.82 Å)] are all close to be reported in Co(dpa)$_2$[29]. The view of the 1D linear chain is shown in Fig. 2.

For complex **2**, As can be seen from Fig. 3, complex **2** is also a monomer with one ligand coordinated to two triorganotin moieties, but different from complex **1**, all the Sn atoms are five-coordinate with a trigonal bipyramidal structure by

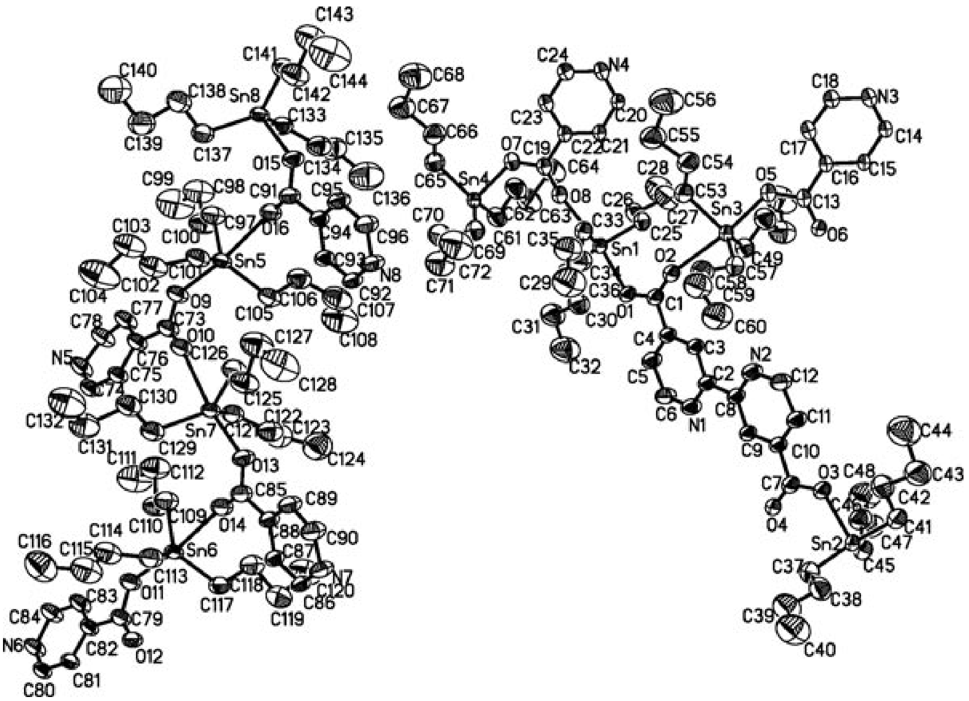


FIGURE 5 The molecular structure of complex **4**.

coordinating an additional methanol group. The Sn(1)–O(1) distance [2.123(4) Å] approaches the sum of the covalent radii of Sn and O(2.13 Å).The axial angle [O(1)–Sn(1)–O(3) = 170.25(17)°] suggests that the structure is near to a normal trigonal bipyramid.

As shown in Fig. 4, owing to the coordinated methanol molecules, a pair of intermolecular O—H···O hydrogen bonds is recognized. Intermolecular hydrogen bond interactions between the methanol and the oxygen atom of an adjacent molecule result in the formation of a 2D network. This is similar to that found in 1,3,5-benzenetricarboxylic acid with trimethyltin chloride [30], The O···O distance, H···O distance, and the O—H···O angle are 2.709, 1.969 and 149.61 Å, respectively.

Structures of Complex **4**. The molecular structures and 2D polymeric structures of complexes **4** are illustrated in Figs. 5 and 6, and selected bond lengths and bond angles are given in Table 4, respectively.

As can be seen from Fig. 5, complex **4** consists of two discrete units, conformations of the two independent units are almost the same, with only little differences in bond lengths and angles (see Table 4). We take molecule A for example, the tri-*n*-butyltin (IV) groups are linked by a carboxylate of each ligand in turn, employing its two bipyridine carboxylic groups to coordinate to four metal centers. Thus, four ligands are linked by four metal centers into a 30-membered macrocycle, which is further linked to eight nearest-neighbor tin centers by a lattice 2D network (see Fig. 6) with a cavity that can be evaluated by the transannular Sn···Sn distances, which are 9.374–16.246 Å. Similar cavities have been found within the polymeric crystal structures of microporous metal–organic frameworks formed between 1,3,5-benzenetricarboxylic acid and Sn [30] and Co [31] centers. All the tin atoms possess the same coordination environment. The coordination about the tin atom is only slightly distorted from the regular trigonal bipyramidal geometry. The Sn—O distances [Sn(1)–O(1) 2.161(7), Sn(2)–O(3) 2.149(8), Sn(3)–O(5) 2.163(8), and Sn(4)–O(7) 2.157(8) Å], together with the other Sn—O distance [Sn(1)–O(8) 2.575(11), Sn(2)–O(6)(symmetry code: 1-*x*, 2-*y*, -*z*) 2.566, Sn(3)–O(2) 2.594(11), and Sn(4)–O(4) (symmetry code: 1-*x*, 1-*y*, -*z*) 2.600 Å] are all lie between the covalent bond length and the van der Waals radii. The O—Sn—O angles [O(1)–Sn(1)–O(8) 171.3(3), O(3)–Sn(2)–O(6) 171.20, O(5)–Sn(3)–O(2) 172.3(3), and O(4)–Sn(4)–O(7) 171.93°] are close to linear arrangement. The sum of the angles subtended at the tin atoms in the equatorial plane is 356.8° for Sn(1), 357.1° for Sn(2), 357.6° for Sn(3), and 361° for Sn(3) so that the atoms [Sn(1), C(25),

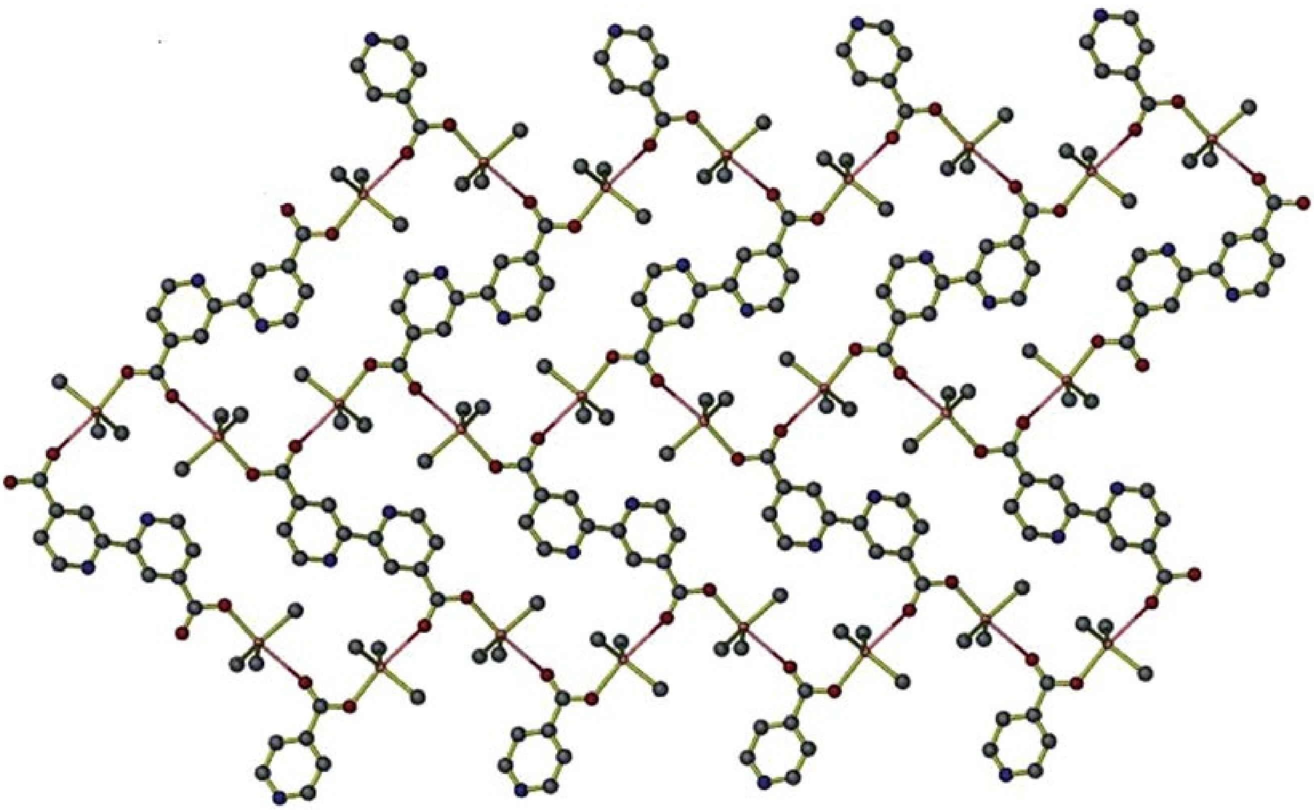


FIGURE 6 The 2D network structure of complex **4** (the β, γ, and δ carbon atoms of the Sn-butyl groups are omitted for clarity).

C(29), C(33)], [Sn(2), C(31), C(47), C(45)], [Sn(3), C(49), C(53), C(57)], and [Sn(4), C(61), C(65), C(69)] are all almost in the same plane.

CONCLUSIONS

In summary, a series of triorganotin (IV) complexes based on 2,2′-bipyridine-4,4′-dicarboxylic acid have been synthesized and characterized. In the crystals, complexes **1** and **2** are monomers, in contrast to complexes **3** and **4** forming 2D polymeric networks, which maybe caused by steric hindrance due to the presence of phenyl and benzyl groups. In addition, weak but significant intermolecular interactions (C—H···N and O—H···O) are observed. Therefore, multidimension self-assembly supramolecular structure is apt to form. At last, the nitrogen atoms in the bipyridine ring of ligand have no obvious influence on the coordination to the central tin atom.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structure analysis of the compounds have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 683177 **1**, 683178 **2**, 699165 **4**. Copies of these information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (http://www.ccdc.cam.ac.uk; Fax: +44-1223-336033).

REFERENCES

[1] Holmes, R. R. Acc Chem Res 1989, 22, 190.

[2] Tiekink, E. R. T. Appl Organomet Chem 1991, 5, 1.

[3] Tiekink, E. R. T. Trends Organomet Chem 1994, 1, 171.

[4] Chandrasekhar, V.; Nagendran, S.; Baskar, V. Coord Chem Rev 2002, 235, 1.

[5] Holmes, R. R.; Schmid, C. G.; Chandrasekhar, V.; Day, R. O.; Holmes, J. M. J Am Chem Soc 1987, 109, 1408.

[6] Dokorou, V.; Ciunik, Z.; Russo, U.; Kovala-Demertzi, D. J Organomet Chem 2001, 630, 205.

[7] Chandrasekhar, V.; Thirumoorthi, R.; Azhakar, R. Organometallics 2007, 26, 26.

[8] García-Zarracino, R.; Höpfl, H. J Am Chem Soc 2005, 127, 3120.

[9] Wang, L.B., Acta Cryst 2007, E63, m1883.

[10] Ma, C. L.; Han, Y. F.; Zhang, R. F. Dalton Trans 2004, 12, 1832.

[11] Ma, C. L.; Li, J. K.; Zhang, R. F. J Organomet Chem 2006, 691, 1713.

[12] Tynan, E.; Jensen, P.; Kruger, P. E.; Lees, A. C.; Nieuwenhuyzen, M. Dalton Trans 2003, 7, 1223.
[13] Tynan, E.; Jensen, P.; Kelly, N. R.; Kruger, P. E.; Lees, A. C.; Moubaraki, B.; Murray, K. S. Dalton Trans 2004, 21, 3440.
[14] Tynan, E.; Jensen, P.; Lees, A. C.; Moubaraki, B.; Murray, K. S.; Kruger, P. E. Cryst Eng Comm 2005, 7, 90.
[15] Tynan, E.; Jensen, P.; Kelly, N. R.; Kruger, P. E.; Lees, A. C.; Moubaraki, B.; Murray, K. S. Dalton Trans 2004, 3440.
[16] Caspar, R.; Musatkina, L.; Tatosyan, A.; Amouri, H.; Gruselle, M.; Guyard-Duhayon, C.; Duval, R.; Cordier, C. Inorg Chem 2004, 43, 7986.
[17] Caspar, R.; Amouri, H.; Gruselle, M.; Cordier, C.; Malezieux, B.; Duval, R.; Levwque, H. Eur J Inorg Chem 2003, 499.
[18] Coronado, E.; Galan-Mascaros, J. R.; Marti-Gastaldo, C.; Palomares, E.; Durrant, J.R.; Vilar, R.; Gratzel, M.; Nazeeruddin, M. K. J Am Chem Soc 2005, 127, 12351.
[19] Wu, J. Y.; Yeh, T. T.; Wen, Y. S.; Twu, J.; Lu, K. L. Cryst Growth Des 2006, 6, 467.
[20] Stocco, G., Guli, G., Girasolo, M. A., Bruno, G., Nicolò, F., Scopelliti, R. Acta Cryst 1996, C52, 829–832.
[21] Sisido, K.; Takeda, Y.; Kinugawa, Z. J Am Chem Soc 1961, 83, 538.
[22] Holmes, R. R.; Schmid, C. G.; Chandrasekhar, V.; Day, R. O.; Homels, J. M. J Am Chem Soc 2000, 122, 5158.
[23] Sandhu, G. K.; Hundal, R. J Organomet Chem 1991, 412, 31.
[24] Holecek, J.; Nadvornik, M.; Handlir, K.; Lycka, A. J organomet Chem 1986, 315, 299.
[25] Vollano, J. F.; Day, R. O.; Rau, D. N.; Chandrasekhar, V.; Holmes, R. R. Inorg Chem 1984, 23, 3153.
[26] Bondi, A. J Phys Chem 1964, 68, 441.
[27] Molloy, K. C.; Purcell, T. G.; Quill, K.; Nowell, I. W. J Organomet Chem 1984, 267, 237.
[28] Forrester, A. R.; Garden, S. J.; Howie, R. A.; Wardell, J. L. J Chem Soc Dalton Trans 1992, 2165.
[29] Cotton, F. A.; Daniels, L. M.; Jordan IV, G. T.; Murillo, C. A. Chem Commun 1997, 1673.
[30] Ma, C. L.; Han, Y. H.; Zhang, R. F.; Wang, D. Q. Eur J Inorg Chem 2005, 3024.
[31] Yaghi, O. M.; Li, G.; Li, H. Nature 1995, 378, 703.