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Synthesis, crystal structures and spectral characterization of diorganotin compounds with phenylglyoxylic acid isonicotinyl hydrazone

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ABSTRACT

The synthesis and characterization of three organotin(IV) compounds with phenylglyoxylic acid isonicotinyl hydrazone (L) are reported. These compounds with the Schiff base ligand of the type – $[R_2SnL_xY_y]_z$ ($x = y = 1$, $z = 2$: $R_1 = CH_3$, Y_1 = EtOH for compound **1** or $R_2 = C_6H_5$, $Y_2 = H_2O$ for compound **2**; and $x = 2$, $y = 0$, $z = 1$, $R = n\text{-}C_4H_9$ for compound **3**) are characterized by IR, ^{1}H, ^{13}C NMR and elemental analysis. The crystal structures of the Schiff base ligand and the corresponding compounds have been determined by X-ray diffraction. In compounds **1** and **2**, the tin atom is seven-coordinate in a distorted pentagonal bipyramid geometry chelating by the Schiff base ligand in an enolic tridentate fashion, forming a Sn_2O_2 ring, only with different coordinated solvent, water for **2** and ethanol for **1**. However, in compound **3**, there exists two different coordinate modes for the same ligand, one type of the usual enolic tridentate and the other type of unique carboxylate monodentate coordination without the participation of the amide group, this results in the central tin atom presenting six-coordinate in a distorted octahedron geometry. Fascinatingly, the supramolecular infrastructures were observed in the Schiff base ligand and three compounds, which exist either as two-dimensional sheets or as three-dimensional networks assembled from the organometallic subunits through intermolecular O—H···X or C—H···X (X=O or N) hydrogen bonds.

1. Introduction

Since some organotin(IV) compounds were synthesized, they have attracted more and more attention in their characteristics, such as pharmic value, anti-tumor activity, and biological activity. In general, the biochemical activity of organotin compounds is influenced greatly by the structure of the molecule and the coordination number of the tin atom [1–3]. They are widely used in microelectronics, nonliner optics, catalysis, host–guest chemistry. For some time, diorganotin compounds are being investigated for their anti-tumor activity [4,5]. The diorganotin (IV) anti-tumor compounds are of tetracoordinated (R_2SnX_2), pentacoordinated (R_2SnY, where Y is a tridentate ligand), and hexacoordinated ($R_2SnX_2L_2$, R = ethyl, n-butyl or phenyl group) geometries [6]. Non-covalent weak molecular forces capable of connecting these metallic subunits into looser and more intriguing supramolecular infrastructures (such as hydrogen bonds, Van der Waals forces, nonbonded contacts, and π–π interactions) [7]. The latter aspect has been actively investigated by a large number of researchers, and a multitude of structural types, including monomers, dimers, tetramers, oligomeric ladders, and hexameric drums, have been discovered [8–13].

Organotin(IV) compounds with Schiff bases have received increasing attention owing to their anti-tumor activities and potential applications in biotechnology [14–20]. In addition, Schiff base organotin(IV) compounds are of interest for structural reasons. The coordination chemistry of some tridentate ONO- and ONS-donor Schiff bases has been described [21,22], and in this paper we report the synthesis and characterization of three new organotin(IV) compounds with Schiff base ligand – phenylglyoxylic acid isonicotinyl hydrazone (L). Their chemical formulas are $[(CH_3)_2Sn(C_{14}H_9N_3O_3)(C_2H_5OH)]_2$ (**1**), $[(C_6H_5)_2Sn(C_{14}H_9N_3O_3)(H_2O)]_2$ (**2**), $[(C_4H_9)_2Sn(C_{14}H_{10}N_3O_3)_2]$ (**3**). The compounds have been characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy. Interestingly, X-ray diffraction analyses demonstrate that different coordination modes for the ligand have been observed in these three compounds although the same reagents and experimental conditions being adopted, which may be due to the different reaction molar ratio of ligand and alkyltin salt compared with those of compounds **1** and **2**. Fascinatingly, the supramolecular infrastructures were observed in the Schiff base ligand and three compounds, which exist either as two-dimensional sheets or as three-dimensional networks assembled from the organometallic subunits through intermolecular O—H···X or C—H···X (X = O or N) hydrogen bonds.

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2. Experimental

2.1. Materials and measurements

Dimethyltin chloride, di-*n*-butyltin chloride, diphenyltin chloride, isonicotinyl hydrazide, phenylglyoxylic acid were commercially available and used without further purification. All the solvents used in the reaction were of analytical grade and were dried before use.

Infrared-spectra were recorded on a Nicolet-460 spectrophotometre using KBr discs and sodium chloride optics, ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400 MHz. The TMS was used as internal standard. The chemical shifts were given in ppm in $CDCl_3$ solvent. Elemental analyses were performed with a PE-2400 II elemental analyser.

2.2. Synthesis of Schiff base ligand – phenylglyoxylic acid isonicotinyl hydrazone

In typical procedure, isonicotinyl hydrazide (1.37 g, 10 mmol) and phenylglyoxylic acid (1.80 g, 10 mmol) was added in CH_3OH (60 ml). The mixture was mechanically stirred and reflux for 4 h. After evaporation of the solvent, the crude product was collected, it was washed first with ethanol and then with dichloromethane–ethanol. For some time, yellow single crystal was formed. Yield: 85%, m.p. 483–485 K. Anal. Calc. for $C_{14}H_{11}N_3O_3$: C 62.45, H 4.12, N 15.61%. Found: C 62.63, H 4.06, N 15.55%. (see: Scheme 1).

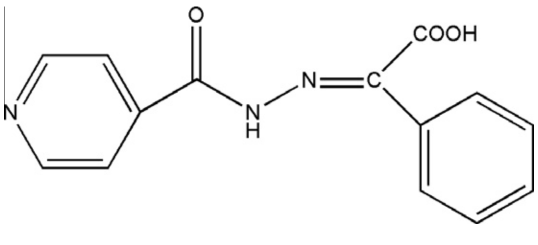
2.3. Synthesis of the organotin(IV) compounds

2.3.1. Preparation of $[(CH_3)_2Sn(C_{14}H_9N_3O_3)(C_2H_5OH)]_2$ (**1**)

The reaction was carried out under nitrogen atmosphere with the use of standard Schlenk technique. The phenylglyoxylic acid isonicotinyl hydrazone (0.1077 g, 0.4 mmol) was added to a solution of absolute ethanol (30 ml) with sodium ethoxide (0.0274 g, 0.4 mmol), the mixture was stirred for half an hour, $(CH_3)_2SnCl_2$ (0.0677 g, 0.4 mmol) was added, stirring for 6 h under refluxing. After cooling down to room temperature, filtrated it and evaporation to dryness, the solid was then recrystallized from dichloromethane–ethanol and yellow single crystal was formed by slow evaporation at room temperature. Yield: 72%. Anal. Calc. for $C_{36}H_{42}N_6O_8Sn_2$: C 46.79, H 4.59, N 9.09%. Found: C 46.62, H 4.54, N 9.03%. ^{1}H NMR ($CDCl_3$, δ ppm): 0.97 (t, 12H, —CH_3), 1.42 (t, 6H, —CH_2—CH_3), 3.67 (m, 4H, —O—CH_2—), 8.53 (s, 2H, —OH), 7.25–7.60 (m, 10H, —C_6H_5), 8.00–8.83 (m, 8H, —C_5H_4N). ^{13}C NMR ($CDCl_3$, 400 MHz): 173.20 (COO), 163.08, 140.60 (C=N—N=C), 47.34 (—OCH_2), 21.93 (—CH_2—CH_3), 149.66, 149.66, 140.60, 125.07, 125.07 (—C_5H_4N), 132.27, 131.18, 130.13, 130.13, 128.23, 128.23 (—C_6H_5), 18.40 (Sn—Me) ppm. IR (KBr, cm^{-1}): 3050 (s, Ar—H), 1635, 1397 (m, COO), 3434 (s, NH), 1635 (s, C=N), 1617 (s, C=N—N=C), 560 (m, Sn—O), 533 (w, Sn—C), 459 (w, Sn—N).

2.3.2. Preparation of compound $[(C_6H_5)_2Sn(C_{14}H_9N_3O_3)(H_2O)]_2$ (**2**)

Compound **2** was prepared by the similar method as compound **1**. The ligand (0.1077 g, 0.4 mmol) was added to the mixture of ethanol and toluene (v/v = 1/3) (30 ml) with sodium ethoxide (0.0274 g, 0.4 mmol), the mixture was stirred for half an hour, $(C_6H_5)_2SnCl_2$ (0.1375 g, 0.4 mmol) was then added, and the reaction mixture was refluxed for 10 h and then filtered and evaporated to dryness under vacuum to form a yellow solid, and then recrystallized from dichloromethane–hexane to give yellow single crystal. Yield: 75%. Anal. Calc. for $C_{52}H_{42}N_6O_8Sn_2$: C 55.95, H 3.79, N 7.53%. Found: C 56.12, H 3.68, N 7.45%. ^{1}H NMR ($CDCl_3$, δ ppm): 6.85–6.97 (m, 20H, —C_6H_5), 7.30–7.62 (m, 10H, —C_6H_5), 8.01–8.80 (m, 8H, —C_5H_4N). ^{13}C NMR ($CDCl_3$, 400 MHz): 173.31 (COO), 163.09, 140.94 (C=N—N=C), 150.20, 150.20, 140.11, 122.09, 122.09 (—C_5H_4N), 132.23, 131.18, 129.39, 129.39, 127.77, 127.77 (—C_6H_5), 137.52, 137.52, 130.25, 128.84, 128.84, 128.84 (Sn—C_6H_5) ppm. IR (KBr, cm^{-1}): 3058 (s, Ar—H), 1625, 1380 (m, COO), 3441 (s, NH), 1660 (s, C=N), 1604 (s, C=N—N=C), 565 (m, Sn—O), 532 (w, Sn—C), 472 (w, Sn—N).



Scheme 1. Schiff base.

2.3.3. Preparation of compound $[(n\text{-}C_4H_9)_2Sn(C_{14}H_{10}N_3O_3)_2]$ (**3**)

Compound **3** was prepared using the procedure as following described. The ligand (0.1077 g, 0.4 mmol) and sodium ethoxide (0.0274 g, 0.4 mmol) were added in the mixture of ethanol and benzene (v/v = 2/1, 30 ml) and heated in standard Schlenk technique, and the mixture was stirred for 20 min. $(n\text{-}C_4H_9)_2SnCl_2$ (0.0608 g, 0.2 mmol) was then added to the mixture, and the reaction was refluxed for 8 h. The solution was filtered and the solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from dichloromethane to give yellow single crystal. Yield: 68%. Anal. Calc. for $C_{36}H_{38}N_6O_6Sn$: C 56.20, H 4.98, N 10.92%. Found: C 56.32, H 4.92, N 10.85%. ^{1}H NMR ($CDCl_3$, δ ppm): 0.91 (t, 6H, —CH_3), 1.37–1.42 (m, 8H, —CH_2CH_2—), 1.68–1.82 (m, 4H, Sn—CH_2—), 7.26–7.59 (m, 10H, —C_6H_5), 7.99–8.80 (m, 8H, —C_5H_4N), 8.60 (s, ^{1}H, —NH), 11.65 (s, ^{1}H, —NHN= =). ^{13}C NMR ($CDCl_3$, 400 MHz): 175.31 (COO), 163.01, 152.94 (C=N—N=C), 149.43, 149.43, 140.94, 122.39, 122.39 (—C_5H_4N), 132.30, 130.10, 128.43, 128.43, 127.80, 127.80 (—C_6H_5), 26.75, 26.46, 21.93, 13.46 (n-C_4H_9—Sn) ppm. IR (KBr, cm^{-1}): 3065 (s, Ar—H), 1637, 1384 (m, COO), 3436 (s, NH), 1637 (s, C=N), 1600 (s, C=N—N=C), 570 (m, Sn—O), 540 (w, Sn—C), 470 (w, Sn—N).

Table 1
Crystal data and structure refinement parameters for the ligand.

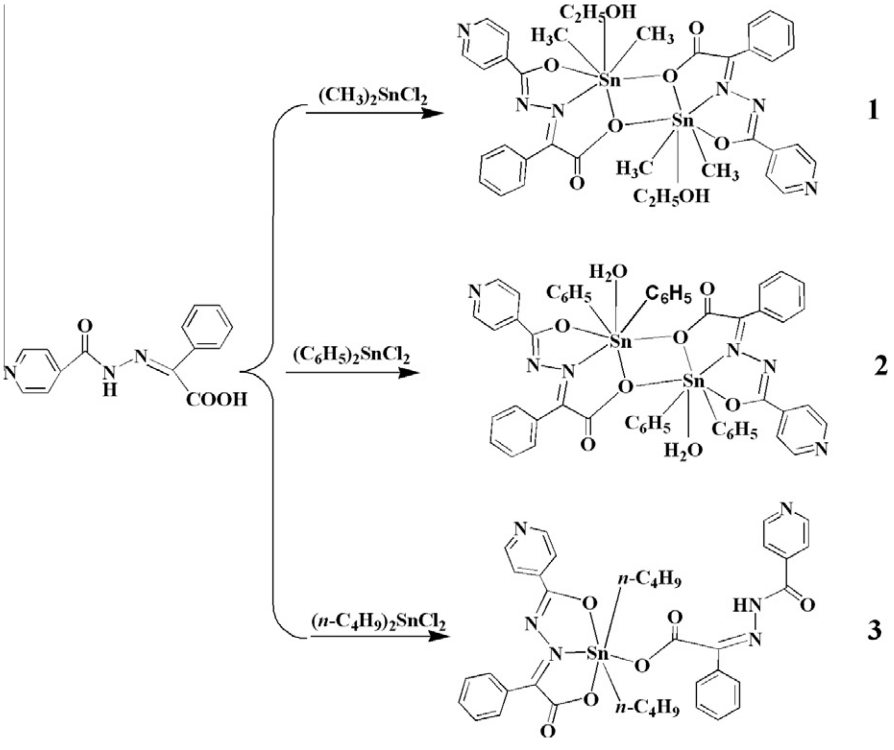
Empirical formula	$C_{14}H_{11}N_3O_3$
Formula weight	269.26
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	
a (Å)	7.3422(7)
b (Å)	17.5751(2)
c (Å)	10.4566(1)
β (°)	110
Volume ($Å^3$)	1267.5(2)
Z	4
Calculated density (mg/m^3)	1.411
Absorption coefficient (mm^{-1})	0.102
F(0 0 0)	560
Crystal size (mm)	0.40 × 0.24 × 0.16
Theta range for data collection (°)	2.32–25.01
Limiting indices	$-6 \leqslant h \leqslant 8$, $-19 \leqslant k \leqslant 20$, $-12 \leqslant l \leqslant 6$
Reflections collected/unique	6320/2241 [*R*(int) = 0.1184]
Completeness to theta = 25.01	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9838 and 0.9602
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2241/0/181
Goodness-of-fit on F^2	1.017
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0592, wR_2 = 0.1149
R indices (all data)	R_1 = 0.1030, wR_2 = 0.1290
Largest diff. peak and hole (e $Å^{-3}$)	0.342 and −0.243

2.4. X-ray crystallography

Crystallographic data and refinement details are given in Tables 1 and 2. All X-ray diffraction pattern were collected on a Bruker SMART CCD 1000 diffractometer. A criterion of observability was used for the solution and refinement. The structure was solved by direct methods (program SHELXL-97 [23]) and refined by a full-matrix least-squares procedure based on F^2 data using the

Table 2
The crystallographic data for compounds **1–3**.

Empirical formula	**1**	**2**	**3**
	$C_{36}H_{42}N_6O_8Sn_2$	$C_{52}H_{42}N_6O_8Sn_2$	$C_{36}H_{38}N_6O_6Sn$
Formula weight	924.14	1116.30	769.41
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	C2/*c*	P2(1)/*n*	Pbca
Unit cell dimensions			
a (Å)	14.9911(15)	9.7108(10)	16.6980(17)
b (Å)	9.1840(10)	10.3070(11)	20.364(2)
c (Å)	28.419(3)	24.264(2)	21.920(2)
β (°)	96.6470(10)	98.1510(10)	90
Volume (Å^3)	3886.4(7)	2404.0(4)	7453.6(14)
Z	4	2	8
Calculated density (mg/m^3)	1.579	1.542	1.371
Absorption coefficient (mm^{-1})	1.342	1.100	0.736
F(0 0 0)	1856	1120	3152
Crystal size (mm)	0.22 × 0.13 × 0.11	0.42 × 0.30 × 0.17	0.42 × 0.21 × 0.13
Scan range θ (°)	1.44–25.02	2.15–25.02	1.83–25.02
Limiting indices	$-16 \leqslant h \leqslant 17$	$-11 \leqslant h \leqslant 10$	$-19 \leqslant h \leqslant 19$
	$-5 \leqslant k \leqslant 10$	$-11 \leqslant k \leqslant 12$	$-24 \leqslant k \leqslant 24$
	$-33 \leqslant l \leqslant 33$	$-28 \leqslant l \leqslant 28$	$-26 \leqslant l \leqslant 16$
Reflections collected/unique	9860/3435 [*R*(int) = 0.0547]	12,122/4244 [*R*(int) = 0.0347]	37,218/6574 [*R*(int) = 0.0985]
Completeness to theta = 25.02	99.9%	99.9%	100.0%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8664 and 0.7567	0.8351 and 0.6551	0.9104 and 0.7474
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3435/598/258	4244/0/307	6574/1/444
Goodness-of-fit on F^2	1.018	1.070	1.152
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0392$	$R_1 = 0.0332$	$R_1 = 0.0595$
	w$R_2 = 0.0801$	w$R_2 = 0.0707$	w$R_2 = 0.1317$
R indices (all data)	$R_1 = 0.0602$	$R_1 = 0.0518$	$R_1 = 0.1624$
	w$R_2 = 0.0864$	w$R_2 = 0.0823$	w$R_2 = 0.2116$
Largest diff. peak and hole (e Å^{-3})	0.794 and −0.679	0.743 and −0.375	1.153and −0.671



Scheme 2. Synthesis of organotin(IV) compounds.

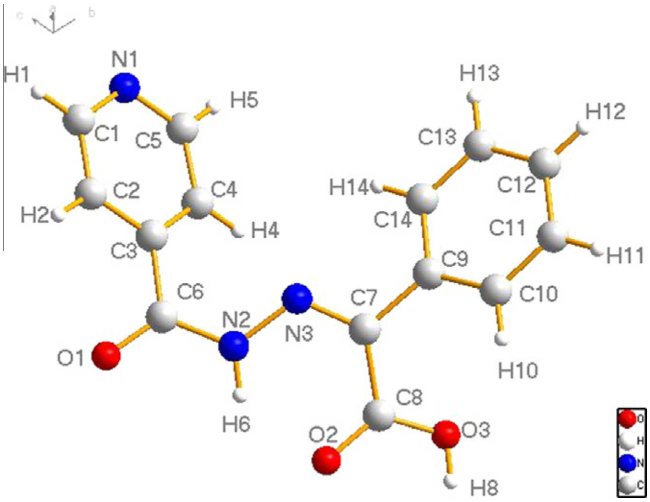


Fig. 1. The molecular structure of Schiff base.

SHELXL-97 [24] program system. All data were collected at 298(2) K using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from geometry of molecules and $\Delta\rho$ maps. During the refinement process they treated as riding atoms [23–26].

3. Results and discussion

3.1. Synthesis of organotin (*IV*) compounds

Compounds **1**–**3** were obtained by the reactions of phenylglyoxylic acid isonicotinyl hydrazone with the alkyltin salt at the presence of sodium ethoxide in different molar ratios and solvent (ethanol for **1**, the mixture of ethanol and toluene for **2** and the mixture of ethanol and benzene for **3**) under the reflux conditions (see Scheme 2). The mixture of the dimethyltin chloride or diphenytin chloride, phenylglyoxylic acid isonicotinyl hydrazone and the sodium ethoxide in the molar ratio of 1:1:1 was found to given the similar molecule structure – dimer, the tin atom is seven-coordinate in a distorted pentagonal bipyramid geometry. However, when the di-*n*-butyltin chloride and the ligand were added with the molar ratio of 1:2, a unique mononuclear diorganotin(IV) compound **3** were obtained, and the central tin atom is six-coordinate in a distorted octahedron geometry.

Table 3
Selected bond lengths (Å) and angles (°) of the ligand.

O3—C8	1.284(3)	N3—C7	1.292(3)
C6—O1	1.222(3)	C7—C9	1.489(4)
C7—C8	1.522(3)	C8—O2	1.241(3)
C7—N3—N2	119.0(2)	O2—C8—O3	124.8(2)
O2—C8—C7	120.0(2)	O3—C8—C7	115.1(3)

3.2. IR spectra

The IR spectra of organotin Schiff base compounds provide useful information about the coordination of the functional groups. The data show the metal–ligand bonds formation through $—CO_2—$, —O— and —N sites, and the associated Sn—O—Sn, Sn—O and Sn—N absorption values are also support this. The $\Delta\nu[\nu as(CO_2^-)–\nu s(CO_2^-)]$ values (230–282 cm^{-1}) for compounds **1**–**3**, indicate that the carboxylate groups adopt the monodentate coordination mode [27]. The characteristic absorption at 1630–1665 cm^{-1} can indicate the presence of C=N group [28]. The characteristic absorption at 1600–1620 cm^{-1} in the spectra of these compounds indicate the presence of the C=N—N=C group [29], thus indicating the ligand coordinate to the tin centre in an enolic form, which is in accordance with the X-ray structure analysis and their corresponding reaction mechanism.

3.3. ^{1}H and ^{13}C NMR spectra ($CDCl_3$)

All compounds are given good NMR spectra. In the ^{1}H NMR spectra of free ligand, the single resonance for the proton of the —NHN = group is observed at δ = 10.8–12.8 ppm, and is absent in the spectra of the compounds, thus indicating deprotonation of the —NHN = group and conforming that the ligand coordinate to the Sn centre in the enolic form. For all compounds, the spectra show that the chemical shifts of the protons on the aryl group have been assigned reasonably. The ^{1}H NMR spectra of the dimethyltin

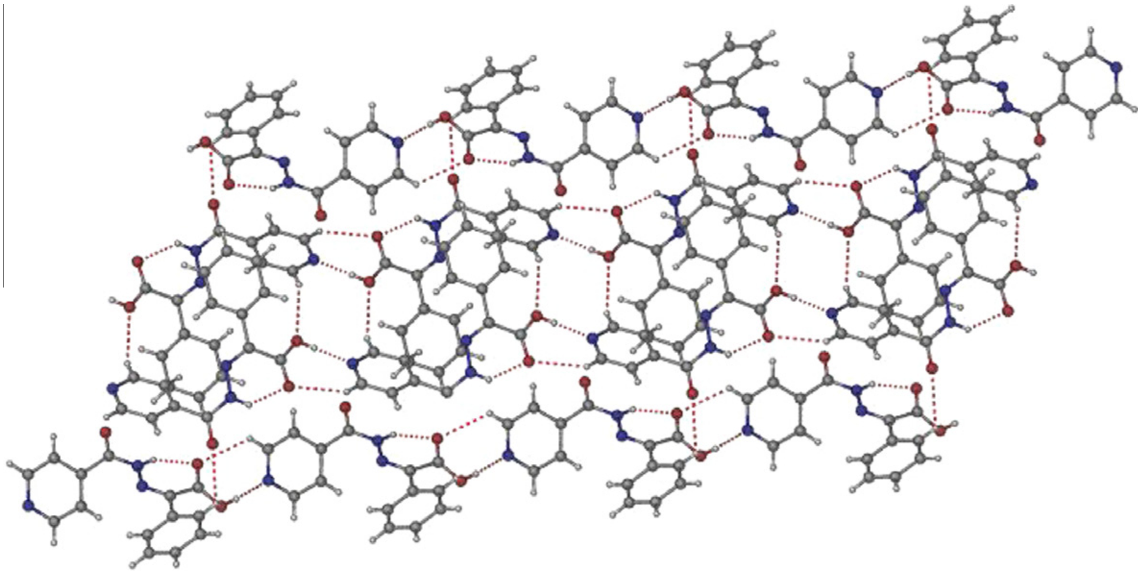


Fig. 2. The two-dimensional sheet of the Schiff base ligand, formed by N—H···O, C—H···O and O—H···N.

Table 4
Geometry parameters of hydrogen bonding geometries for the ligand and compounds **1**–**3**.

Ligand				
D···A	D—H	H···A	D···A	D—H···A
N2—H6···O2	0.86	1.91	2.586(2)	134.0
C1—H1···O2#1	0.93	2.53	3.149(3)	124.2
C5—H5···O3#2	0.93	2.66	3.494(4)	148.9
C10—H10···O1#3	0.93	2.62	3. 239(3)	124.4
O3—H8···N1#4	0.82	1.78	2.596(3)	175.2
*Compound **1***				
D—H···A	D—H	H···A	D···A	D—H···A
O(4)—H(1)···O(2)#1	0.83(9)	1.82(9)	2.625(4)	161(10)
C(4)—H(4)···N(3)#2	0.93	2.72	3.562(6)	150.7
*Compound **2***				
D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O1#1	0.85	2.63	3.121(3)	118.0
O4—H4A···O2#1	0.85	1.78	2.620(4)	172.8
O4—H4B···N3#2	0.86	1.84	2.695(4)	174.0
C22—H22···O3#3	0.93	2.61	3.430(6)	147.5
*Compound **3***				
D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···O5	0.89	2.02	2.710(13)	133.5
N3—H3···O1#1	0.86	2.36	2.990(12)	130.3
N3—H3···O2#1	0.86	2.04	2.888(11)	169.8
C14—H14···O1#1	0.93	2.58	3.107(14)	116.6
C14—H14···O4#1	0.93	2.30	3.200(15)	162.6
C24—H24···O2#2	0.93	2.50	3.390(18)	159.9
C27—H27···O2#3	0.93	2.66	3.192(16)	116.9
C(10)—H(10)···N(4)#4	0.93	2.31	3.238(15)	172.1
C(10)—H(10)···N(6)#5	0.93	3.10	3.248(18)	90.7

Symmetry codes: for Schiff base: #1 *x* + 1, *y*, *z* + 1; #2 − *x*, −*y* + 1, −*z*; #3 *x*, −*y* + 1/2, *z* − 1/2; #4 *x* − 1, *y*, *z* − 1; for compound **1**: #1 − *x*,− *y* + 2, −*z*; #2 − *x* + 1/2, *y* + 1/2, −*z* + 1/2; for compound **2**: #1 − *x*, −*y* + 2, −*z*; #2 − *x* − 1/2, *y* + 1/2, −*z* + 1/2; #3 *x* + 1, *y*, *z*; for compound **3**: #1 − *x* + 1/2, −*y* + 1, *z* + 1/2; #2 − *x* + 1, *y* − 1/2, −*z* + 1/2; #3 − *x* + 1/2, *y* − 1/2, *z*; #4 *x*, −*y* + 1/2, *z* + 1/2; #5 *x* − 1/2, −*y* + 1/2, −*z* + 1.

compound show the signal of Sn—CH_3 at 0.97 ppm. In the ^{13}C NMR spectra of compounds, there contain one or two five-membered ring, and correspondingly, at 140–165 ppm three peaks were observed for the bonding C atoms. The ^{13}C NMR data are consistent with carboxylate structures, the single at 173.20–175.31 ppm. In three compounds, the biggest difference of the ^{13}C NMR come from the change of the alkyl groups bonding with tin centre.

3.4. X-ray crystallography

3.4.1. Crystal structure of Schiff base ligand

The molecular structure and the two-dimensional sheet of Schiff base is shown in Figs. 1 and 2. The crystal data and structure refinement parameters and selected bond lengths and angles are shown in Tables 1 and 3. The H-bonds are given in Table 4. All H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H distances of 0.93 Å and displacement parameters assigned as $U_{iso}(H) = 1.2U_{eq}(C)$. The angle of the C7—N3—N2=C6 is −178.6(2)°, and due to the presence of the lone pair electron for nitrogen atom, it is the conducive to the coordination to the metal centre. The bond lengths O3—C8 and C8=O2 are 1.284(3) and 1.241(3) Å, which are greater shorter than C—O (1.43 Å) and less longer than C=O (1.20 Å). The O3—C8=O2 is considered conjugated system. From the structure, it is inferred that the N and O atoms can participate in the coordination.

In the Schiff base, there are one intramolecular hydrogen bond and four intermolecular hydrogen bonds. The distance of the N2—H6···O2 is 1.91 Å. The distance of the O3—H8···N1#4 (#4*x* − 1, *y*, *z* − 1) is 1.71 Å. The distance of C—H···O is 2.53–2.66 Å. The hydrogen bonds make the Schiff base form two-dimensional laminated structure. Obviously, these H-bonds supply the additional stability effect for the solid-state structure of the Schiff base.

3.4.2. Crystal structures of compounds 1 and 2

The crystallographic data of compounds **1** and **2** are given in Table 2. The molecular structure of the compounds **1** and **2** is shown in Figs. 3 and 4. Compounds **1** and **2** have the similar bridged dimeric structure, which also present the identical structure geometry of trans-C_2SnO_4N pentagonal bipyramid with that of compound **1** for the central tin atom, only with different coordinated solvent, ethanol for **1** and water for **2** and the different alkyl groups, methyl group for **1** and benzyl group for **2**. In other words, the nature the alkyl group and the coordinated solvent molecule bonding to the Sn centre does not play an important role on the structure of bridged dimers. The selected bond lengths and angles are given in Table 5. In compound **1**, the tin atom is surrounded equatorially

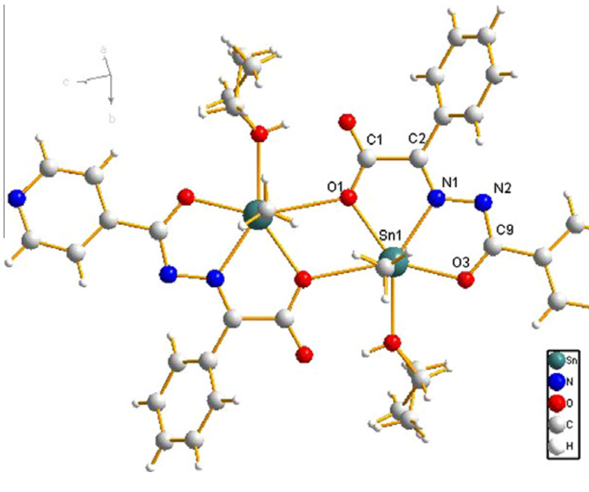


Fig. 3. The molecular structure of compound **1**.

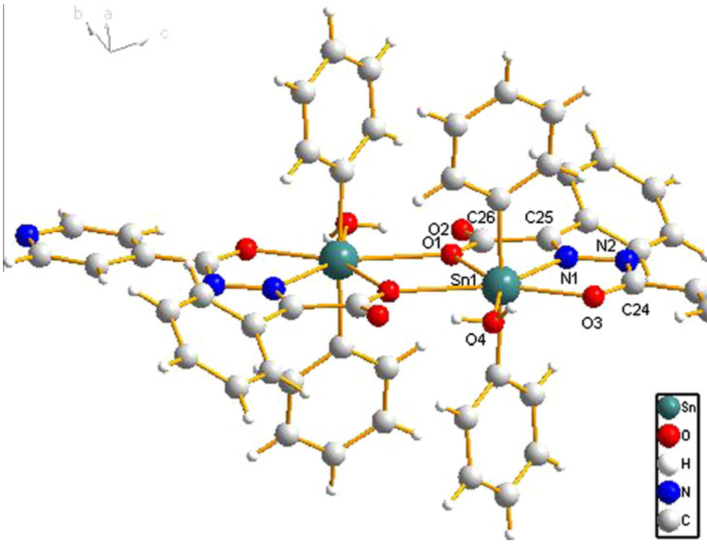


Fig. 4. Crystal structure of compound **2**.

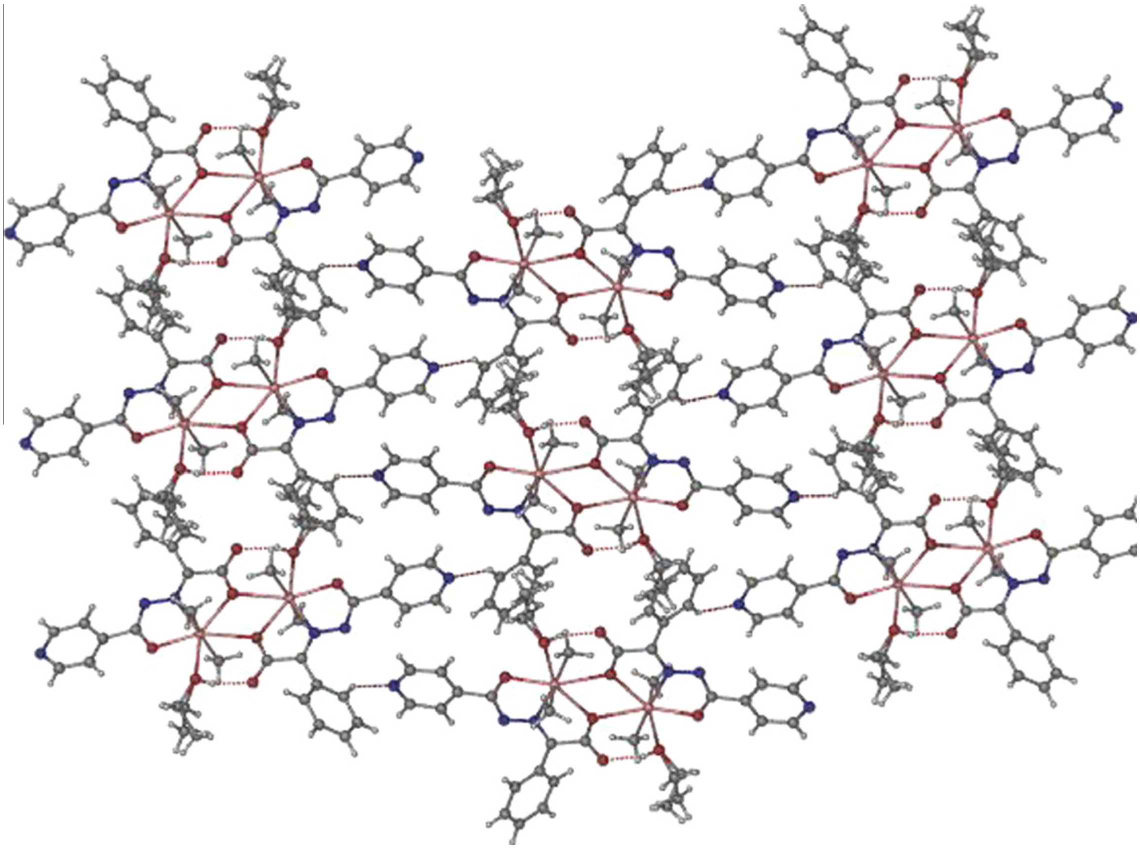


Fig. 5. Two-dimensional sheet structure of compound **1**, formed by O4—H1···O2#1 and C4—H4···N3#2.

by four O atoms and one C atom from the ligand, and the axis position is occupied by two C atoms from the methyl group. The Sn1—C15 distance is 2.096(4) Å, the Sn1—C16 distance is 2.101(5) Å. The angle of C15—Sn1—C16 is 164.08(18)°, which is deviated from linear angle 180°. It is a centrosymmetric arrangement leading to a Sn_2O_2 core connected by the Sn—O bond, and the Sn1—O1#1 bond distance is 2.717(3) Å, is greater than the sum of the covalent radii of Sn and O (2.56 Å), but is considerably less than the sum of the Van der Waals radii Sn—O (3.68 Å), indicating the weak bonding interaction between Sn1 and O1#1. The Sn1—N1 distance is 2.274(3) Å, which is greater longer 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) [30], and should be considered as bonding interactions. It is worth mentioning that the solvent molecule – ethanol involved in the coordination in a disordered structure. In compound **1**, there exists

Table 5
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

*Compound **1***			
Sn1—C15	2.096(4)	Sn1—C16	2.101(5)
Sn1—O3	2.196(3)	Sn1—N1	2.274(3)
Sn1—O1	2.325(3)	Sn1—O4	2.391(3)
Sn1—O1#1	2.717(3)		
C15—Sn1—C16	164.08(19)	O3—Sn1—N1	69.84(11)
N1—Sn1—O1	69.03(10)	O3—Sn1—O4	76.94(11)
O1—Sn1—O1#1	66.09(11)	O4—Sn1—O1#1	78.09(10)
*Compound **2***			
Sn1—C7	2.130(4)	Sn1—C1	2.139(4)
Sn1—O3	2.207(2)	Sn1—O4	2.263(3)
Sn1—N1	2.315(3)	Sn1—O1	2.371(2)
Sn1—O1#1	2.561(2)		
C7—Sn1—C1	173.79(15)	O3—Sn1—O4	75.83(9)
O3—Sn1—N1	69.19(10)	O1—Sn1—O1#1	66.48(10)
N1—Sn1—O1	68.10(9)	O4—Sn1—O1#1	80.39(8)

Symmetry code: (#1 for 1) −*x*, −*y* + 2, −*z*; (#1 for 2) #1 − *x*, −*y* + 2, −*z*.

intermolecular hydrogen bonds O4—H1···O2#1, C4—H4···N3#2, which contribute to the formation of the two-dimensional sheet (Fig. 5).

In compound **2**, the central tin is surrounded equatorial by O1, O1#1, N1, O3 from the ligand and O4 from the solvent molecule – water. The sum of angles N1—Sn1—O1, O3—Sn1—N1, O3—Sn1—O4, O4—Sn1—O1#1 and O1—Sn1—O1#1 subtends at the Sn1 atom in the pentagonal plane is 360°, so O1, O1 #1, N1, O3 and O4 are in the same plane. The benzyl group takes up the axial sites around the Sn1 atom. The angle of the axial C1—Sn1—C7 is 173.77(15) Å. O1 atom of the carboxylate residue also binds the other tin atom, generating a Sn_2O_2 four-membered ring. The distance of Sn1—O1#1 is 2.561(2) Å, close to the sum of the covalent radii of Sn and O (2.56 Å), indicating the strong tin–oxygen interaction. The Sn1—N1 is 2.315(3) Å, which is greater longer 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) [28], and should be considered as the bonding interactions. The intermolecular chains O4—H4A···O1#1 (#1 − *x*, −*y* + 2, −*z*), O4—H4A···O2#1 (#1 − *x*, −*y* + 2, −*z*), C22—H22···O3#3 (#3*x* + 1, *y*, *z*) and O4—H4B···N3#2 (#2 − *x* − 1/2, *y* + 1/2, −*z* + 1/2) hydrogen bonds to generate three-dimensional network (Fig. 6), which makes the compound more stable.

3.4.3. Crystal structure of compound 3

The molecular structure of the compound **3** is shown in Fig. 7. The crystallographic data and selected bond lengths and angles are given in Tables 2 and 6. There was no interaction between the Sn1 atom and O1 atom (Sn1—O1#1). The central tin atom is six-coordinate in a distorted octahedron geometry and the central tin atom is surrounded equatorial by N1, O1, O3, O4 from the ligand and the C29 and C33 from the *n*-butyl group taking up the axial positions. The angle of the axial C33—Sn1—C29 is 156.6(5)°, which is deviated from the linear angle of 180°. The bond length of Sn1—O4 is 2.278(7) Å. The tin atom, the bonded oxygen and nitrogen atoms are nearly coplanar and deviate only slightly from regular square geometry, mean deviation from planar is 0.07 Å. The Sn1—N1 distance, 2.290(9) Å, which is greater than the sum of the

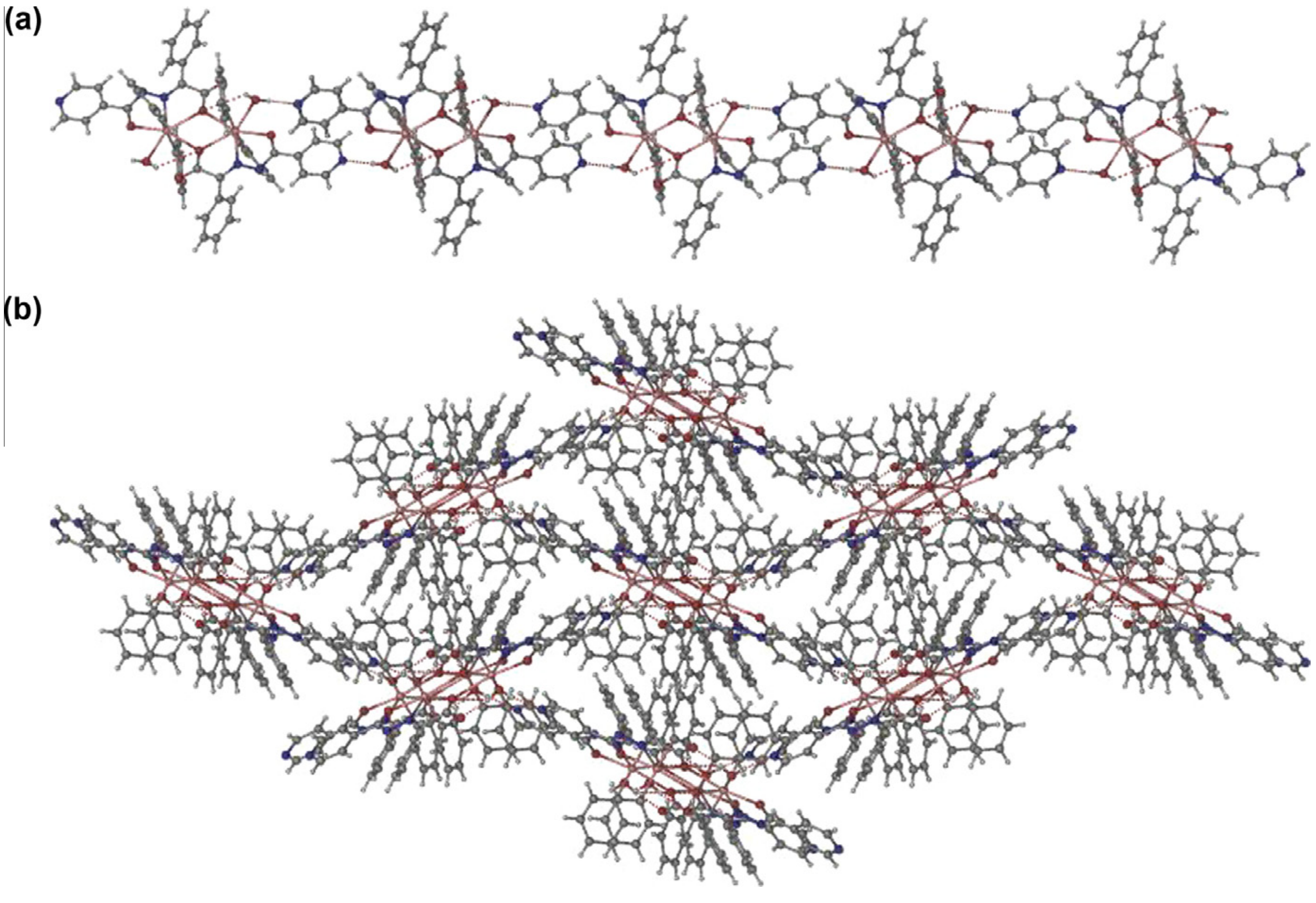


Fig. 6. (a) One-dimensional chain structure of compound **2**, O4—H4A···O1, O4—H4A···O2#1, C22—H22···O3#3; (b) Three-dimensional network of compound **2**, formed by O4—H4A···O1, O4—H4A···O2, C22—H22···O3 and O4—H4B···N3.

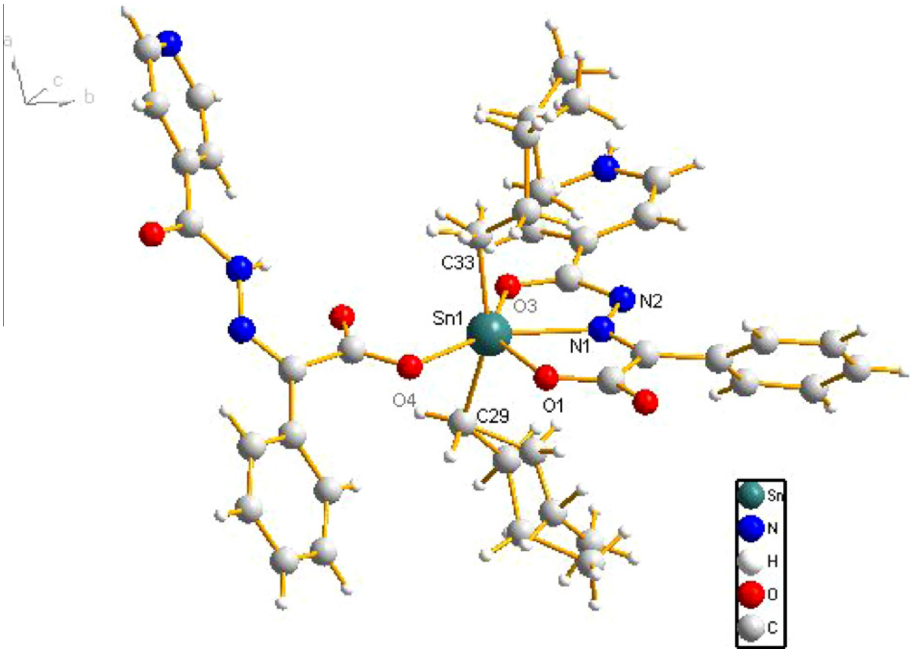


Fig. 7. Crystal structure of compound **3**.

Table 6
Selected bond lengths (Å) and angles (°) for compound **3**.

Sn1—C33	2.089(13)	Sn1—C29	2.124(13)
Sn1—O1	2.152(8)	Sn1—O4	2.278(7)
Sn1—N1	2.290(9)	Sn1—O3	2.308(7)
C33—Sn1—C29	156.6(5)	O1—Sn1—O4	75.3(3)
O1—Sn1—N1	71.0(3)	O4—Sn1—O3	145.8(3)
N1—Sn1—O3	68.0(3)		

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) [28], indicating the strong bond of Sn—N interactions. There are intramolecular N—H···O hydrogen bond and intermolecular C—H···O, C—H···N and N—H···O hydrogen bonds (Table 4), and a three-dimensional network (Fig. 8) is created by them. They create network along the crystallographic [0 1 0] axis.

4. Conclusions

Three new organotin compounds derived from Schiff base – phenylglyoxylic acid isonicotinyl hydrazone have been reported here. Our investigation on the structures and spectra of these compounds indicate that the structures of compound **1** and compound **2** have a distorted pentagonal bipyramid and compound **3** has a distorted octahedron geometry. In compounds **1** and **2**, the central tin atom is seven coordinated, but in compound **3**, the central tin atom is six coordinated. Besides, the *R* groups of the R_2Sn are found

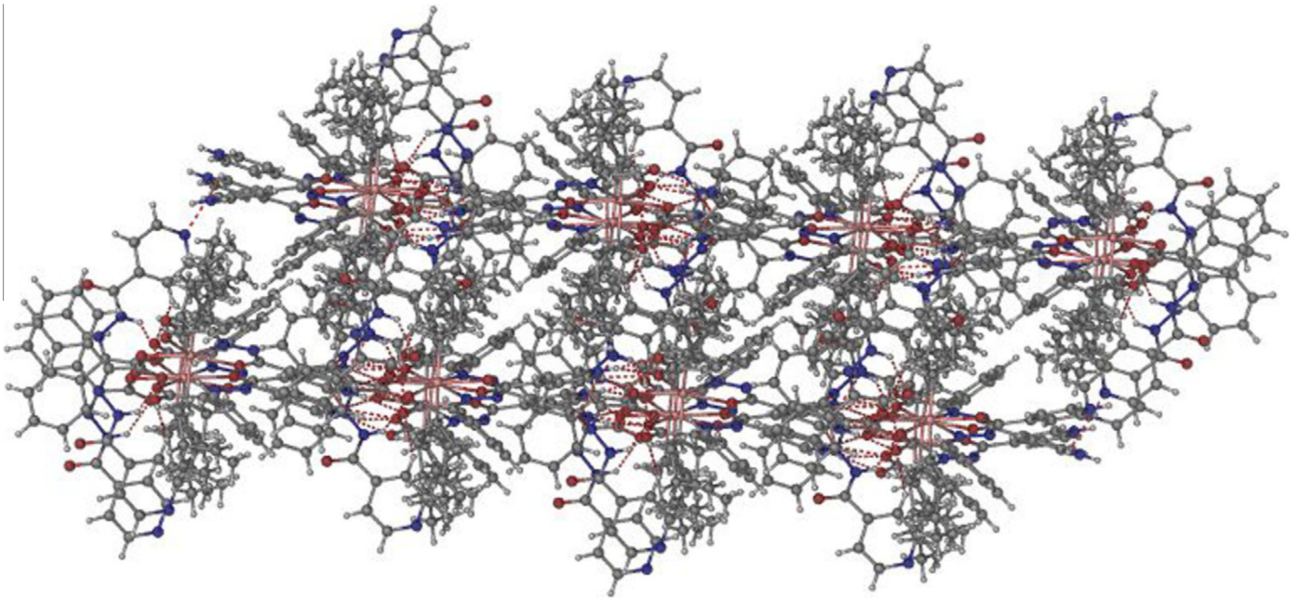


Fig. 8. Three-dimensional network of compound **3**, formed by C—H···N, C—H···O and N—H···O.

to have great influence on the coordination mode. Fascinatingly, the supramolecular infrastructures are observed in the Schiff base ligand and three compounds, which exist either as two-dimensional sheets or as three-dimensional networks assembled from the organometallic subunits through intermolecular O—H···X or C—H···X (X=O or N) hydrogen bonds.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 787024 for Schiff base, Nos. 787022, 787025, 787023 for compounds **1**–**3**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] Q.L. Xie, X.H. Xu, H.G. Wang, X.K. Yao, Z.G. Zhang, J.M. Hu, Acta Chim. Sinica 49 (1991) 1085.
[2] C.J. Evans, R.J. Hill, Oil Color Chem. Assoc. 64 (1981) 215.
[3] S.R. Collinson, D.E. Fenton, Coord. Chem. Rev. 148 (1996) 19.
[4] V. Narayanan, M. Nasr, K.D. Paull, in: M. Gielen (Ed.), Tin-based Anti-tumor Drugs, Springer-Verlag, Berlin, 1990, p. 201.
[5] M. Gielen, Coord. Chem. Rev. 151 (1996) 41.
[6] P. Yang, M. Guo, Coord. Chem. Rev. 186 (1999) 189.
[7] C.L. Ma, Q.F. Zhang, R.F. Zhang, D.Q. Wang, Chem. Eur. J. 12 (2006) 420.
[8] R.R. Holmes, Acc. Chem. Res. 22 (1989) 190.
[9] E.R.T. Tiekink, Trends Organomet. Chem. 1 (1994) 71.
[10] E.R.T. Tiekink, Appl. Organomet. Chem. 5 (1991) 7.
[11] J. Beckmann, D. Dakternieks, A. Duthie, F.S. Kuan, K. Jurkschat, M. Schürmann, E.R.T. Tiekink, New J. Chem. 28 (2004) 1268.
[12] M. Mehring, G. Gabriele, S. Hadjikakou, M. Schürmann, D. Dakternieks, K. Jurkschat, Chem. Commun. (2002) 834.
[13] M. Mehring, I. Paulus, B. Zobel, M. Schürmann, K. Jurkschat, A. Duthie, D. Dakternieks, Eur. J. Inorg. Chem. (2001) 153.
[14] R.S. Collinson, D.E. Ferton, Coord. Chem. Rev. 148 (1996) 19.
[15] P. Yang, M. Guo, Coord. Chem. Rev. 185 (1999) 189.
[16] M. Gielen, Metal-Based Drugs 1 (1994) 213.
[17] M. Nath, S. Pokharia, R. Yadav, Coord. Chem. Rev. 215 (2001) 99.
[18] A.J. Crowe, P.J. Smith, C.J. Cardin, H.E. Parge, F.E. Smith, Cancer Lett. 24 (1984) 45.
[19] V.I. Bregadze, S.A. Glazun, P.V. Petrovakii, Z.A. Starikova, V.Y. Rochev, H. Dalil, M. Biesemans, R. Willem, M. Gielen, D.D. Vos, Appl. Organomet. Chem. 17 (2003) 453.
[20] K.C. Joshi, V.N. Pathak, P. Panwar, Agric. Biol. Chem. 41 (1977) 543.
[21] A. Saxena, J.P. Tandon, A.J. Crowe, Polyhedron 4 (1985) 1085.
[22] G.Y. Yeap, H.K. Fun, S.B. Teo, S.G. Teoh, Acta Crystallogr. C48 (1992) 1109.
[23] M. Sheldrick, Acta Crystallogr. A46 (1990) 467.
[24] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
[25] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, A Progrom for the Automated Generation of a Variety of Geometrical Entities, Utrecht University, Utrecht, The Netherlands, 2001.
[26] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.
[27] M. Gielen, H. Dalil, L. Ghys, B. Boduszek, E.R.T. Tiekink, J.C. Martins, M. Biesemans, R. Willem, Organometallics 17 (1998) 4259.
[28] D.K. Rastogi, S.K. Dua, V.B. Rana, S.K. Shni, J. Indian Chem. Soc. (1978) 1323.
[29] H.D. Yin, M. Hong, G. Li, S.C. Xue, D.Q. Wang, J. Organomet. Chem. 690 (2005) 1669.
[30] A. Bondi, J. Phys. Chem. 68 (1964) 441.