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Isothiocyanatotriphenyl(pyridinium-2-carboxylato)tin(IV) Monohydrate*

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Abstract

The crystal structure of isothiocyanatotriphenyl-(pyridinium-2-carboxylato)tin(IV) monohydrate is reported. The crystals are monoclinic, space group $P2_1/n$, a = 10.349(2), b =12.003(2), c = 19.325(4) Å, β = 97.68(2)°, Z = 4, refined to R_F = 0.024 on 4249 observed reflections.

The tin(IV) atom is five-coordinate, being bound to three phenyl groups, the isothiocyanato nitrogen atom and an oxygen from the picolinic acid. The geometry around the tin atom is trigonal bipyramidal, with the three phenyl groups occupying the equatorial positions, while the picolinic acid oxygen and the isothiocyanato nitrogen are coordinated axially. The acidic proton of picolinic acid has shifted position in the complex, and is bound to the heterocyclic nitrogen atom. The acid is thus coordinated in the form of a zwitterion. These trigonal bipyramidal units are linked together as dimers by pairs of water molecules, each of which hydrogen-bonds to the non-coordinated carboxylate oxygen atoms of both picolinic acid molecules, plus the heterocyclic nitrogen atom of one picolinic acid molecule. For complex formation with the protonated acid, the heterocyclic nitrogen should be *alpha* to the carboxylic acid group.

Introduction

We have recently reported the synthesis and crystal structure of several triphenyltin chloride complexes with the planar and (potentially) bidentate chelating agents: phenanthroline, bipyridine, picolinic acid and quinaldic acid [1–3]. All the compounds show a trigonal bipyramidal geometry around the tin atom and all exist as hydrogen-bonded dimers. In the cases where the ligand is picolinic or quinaldic acid, the ligand exists in the form of a zwitterion, and behaves as a monodentate, being directly bound to the tin via a carboxyl oxygen. Hydrogen bonds involving uncoordinated water molecules, or the zwitterion protons of the ligand, serve to bind the five-coordinate units together in the dimer. On the other hand, in the phenanthroline and bipyridine complexes, it is the water molecule which is coordinated to the tin atom, and the molecules of phenanthroline or bipyridine, which are not directly bound to the metal, bind the monomeric units into the dimer, through hydrogen bonds to the heterocyclic nitrogen atoms.

All the structures have proved to be unusual, which has prompted us to attempt the synthesis of further complexes of triorganotins with potentially bidentate ligands.

We describe here the synthesis and crystal structure of another such complex, that formed between triphenyltin isothiocyanate and picolinic acid.

Experimental

Preparation of the Complex

The reagents pyridine-2-carboxylic acid and triphenyltin chloride were obtained commerically and used without further purification.

An ethanolic solution of triphenyltin isothiocyanate was prepared from the chloride by a metathetical reaction in ethanol with potassium thiocyanate, and the precipitated potassum chloride was filtered off.

The 1:1 complex, Ph_3SnNCS·picolinic acid·H_2O, was obtained as a white crystalline solid in good yield by mixing hot ethanol solutions containing the

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TABLE I. Positional Parameters and Isotropic Thermal Parameters

	x	y	z	B_{iso}
Sn	0.40962(3)	0.332153(23)	0.179926(21)	2.962(17)
S	0.83835(14)	0.22097(11)	0.10385(10)	5.96(10)
O1	0.2204(3)	0.38188(24)	0.21301(21)	3.56(22)
O2	0.1261(4)	0.4351(3)	0.10728(23)	4.8(3)
H20	−0.1625(6)	0.4838(4)	0.0247(3)	5.9(4)
N1	0.6104(4)	0.2928(3)	0.1493(3)	4.5(3)
N2	−0.0839(6)	0.5035(3)	0.1618(4)	3.1(3)
C1	0.0181(6)	0.4735(4)	0.2039(3)	2.9(3)
C2	0.0200(6)	0.4807(4)	0.2754(3)	3.1(3)
C3	−0.0906(6)	0.5209(4)	0.3013(4)	3.1(3)
C4	−0.1951(6)	0.5506(4)	0.2560(4)	4.0(4)
C5	−0.1952(7)	0.5437(4)	0.1836(4)	5.0(5)
C6	0.7049(5)	0.2634(4)	0.1293(3)	3.2(3)
C7	0.1347(6)	0.4252(4)	0.1714(3)	3.1(4)
C1A	0.3239(5)	0.1997(3)	0.1173(3)	3.4(3)
C2A	0.2064(5)	0.1507(4)	0.1324(3)	4.2(3)
C3A	0.1558(6)	0.0592(5)	0.1001(4)	5.2(4)
C4A	0.2117(7)	0.0069(5)	0.0453(5)	4.7(5)
C5A	0.3313(6)	0.0551(5)	0.0306(4)	5.0(4)
C6A	0.3846(5)	0.1469(4)	0.0652(3)	4.0(3)
C1B	0.4399(5)	0.5002(4)	0.1511(3)	3.3(3)
C2B	0.4393(7)	0.5339(4)	0.0823(4)	5.2(4)
C3B	0.4581(7)	0.6456(5)	0.0663(4)	6.5(5)
C4B	0.4802(8)	0.7232(4)	0.1185(5)	6.1(6)
C5B	0.4813(8)	0.6911(4)	0.1868(4)	5.7(5)
C6B	0.4592(5)	0.5801(4)	0.2027(3)	4.2(3)
C1C	0.4729(6)	0.2978(4)	0.2854(4)	3.1(4)
C2C	0.6019(13)	0.3165(5)	0.3168(7)	5.4(6)
C3C	0.6409(14)	0.3011(6)	0.3871(7)	6.0(8)
C4C	0.5516(12)	0.2624(7)	0.4287(8)	8.9(8)
C5C	0.4274(12)	0.2419(5)	0.4014(8)	6.0(6)
C6C	0.3876(9)	0.2574(4)	0.3310(5)	4.7(4)
HN2	−0.083(9)	0.495(5)	0.102(5)	5.9(13)
H2	0.107	0.454	0.311	4.1
H3	−0.097	0.529	0.355	4.0
H4	−0.281	0.580	0.277	5.9
H5	−0.283	0.570	0.145	5.9
H2A	0.151	0.191	0.170	5.1
H3A	0.074	0.027	0.122	6.5
H4A	0.167	−0.069	0.016	5.9
H5A	0.388	0.020	−0.008	5.8
H6A	0.478	0.177	0.052	5.5
H2B	0.416	0.470	0.038	5.6
H3B	0.464	0.671	0.013	6.5
H4B	0.495	0.812	0.105	7.5
H5B	0.509	0.750	0.232	5.9
H6B	0.449	0.556	0.256	4.6
H2C	0.672	0.341	0.283	5.3
H3C	0.747	0.319	0.410	6.8
H4C	0.581	0.248	0.487	8.9
H5C	0.352	0.219	0.432	7.0
H6C	0.285	0.237	0.310	6.3

e.s.d.s refer to the least significant digit quoted. In order to preserve significance on small values, e.s.d.s less than 25 are quoted with two digits. For non-hydrogen atoms, B_{iso} is the arithmetic mean of the principal axes of the thermal ellipsoid.

stoichiometric quantities of triphenyltin isothiocyanate and picolinic acid. The complex crystallised from ethanol.

Microanalyses were performed at the National University of Singapore. *Anal.* for Ph$_3$SnNCS·picolinic acid·H$_2$O: Calc. for $C_{25}H_{22}N_2O_3SSn$: C, 54.67; H, 4.04; N, 5.10; Sn, 21.61. Found: C, 55.01; H, 3.67; N, 5.02; Sn, 21.5%.

Crystal Data

Monoclinic Space group $P2_1/n$; a = 10.349(2), b = 12.003(2), c = 19.325(4) Å, β = 97.68(2)°, Z = 4, D_c = 1.53 Mg m^{-3}, μ = 1.19 mm^{-1}.

Intensity Data

The diffraction intensities of an approximately 0.2 × 0.3 × 0.3 mm dimensions crystal were collected with graphite monochromatised Mo Kα radiation, using the $\theta/2\theta$ scan technique with profile analysis [4] to $2\theta_{max}$ = 55°. A total of 5473 unique reflections were measured, of which 4249 reflections were considered significant, with $I_{net} > 2.5\sigma(I_{net})$. Lorentz and polarisation factors were applied, but absorption correction was unnecessary (μ = 1.19 mm^{-1}). The cell parameters were obtained by least-squares refinement of the setting angles of 68 reflections when $2\theta > 50°$ ($\lambda_{MoK\alpha}$ = 0.70932 Å).

Structure Solution and Refinement

The structure was solved by direct methods and refined with full-matrix least-squares. Where possible, H atom positions were calculated, and their parameters were not refined. The hydrogen atom HN2 was located in a D-map, and its position refined isotropically. All heavier atoms were refined anisotropically. The final residuals are R_F = 0.024 and R_w = 0.018 for the significant data (R_F = 0.039 and R_w = 0.018 for all data). Weights based on counting statistics were used throughout. All calculations were performed with the NRC VAX system of programs [5]. Literature values were used for the scattering factors [6].

TABLE II. Bond Distances (Å) and Angles (°).

Distances (Å)		Angles (°)	
Sn–O(1)	2.221(2)	O(1)–Sn–N(1)	175.8(2)
Sn–N(1)	2.284(3)	O(1)–Sn–C(1A)	92.8(1)
Sn–C(1A)	2.119(6)	O(1)–Sn–C(1B)	89.3(1)
Sn–C(1B)	2.127(4)	O(1)–Sn–C(1C)	86.9(1)
Sn–C(1C)	2.097(9)	N(1)–Sn–C(1A)	91.3(2)
S–C(6)	1.610(3)	N(1)–Sn–C(1B)	87.6(1)
O(1)–C(7)	1.229(9)	N(1)–Sn–C(1C)	92.0(2)
O(2)–C(7)	1.237(8)	C(1A)–Sn–C(1B)	128.9(2)
N(1)–C(6)	1.155(4)	C(1A)–Sn–C(1C)	117.4(2)
N(2)–C(1)	1.294(11)	C(1B)–Sn–C(1C)	113.8(2)
N(2)–C(5)	1.367(6)	Sn–O(1)–C(7)	120.8(2)
C(1)–C(2)	1.382(9)	Sn–N(1)–C(6)	172.2(5)
C(1)–C(7)	1.546(5)	C(1)–N(2)–C(5)	123.6(6)
C(2)–C(3)	1.395(5)	N(2)–C(1)–C(2)	120.9(4)
C(3)–C(4)	1.345(11)	N(2)–C(1)–C(7)	117.6(5)
C(4)–C(5)	1.401(10)	C(2)–C(1)–C(7)	121.5(7)
C(1A)–C(2A)	1.416(5)	C(1)–C(2)–C(3)	118.5(7)
C(1A)–C(6A)	1.408(5)	C(2)–C(3)–C(4)	119.1(6)
C(2A)–C(3A)	1.335(9)	C(3)–C(4)–C(5)	121.8(4)
C(3A)–C(4A)	1.420(7)	N(2)–C(5)–C(4)	116.2(8)
C(4A)–C(5A)	1.428(7)	S–C(6)–N(1)	178.2(7)
C(5A)–C(6A)	1.366(9)	O(1)–C(7)–O(2)	130.2(4)
C(1B)–C(2B)	1.390(9)	O(1)–C(7)–C(1)	115.3(5)
C(1B)–C(6B)	1.379(8)	O(2)–C(7)–C(1)	114.5(6)
C(2B)–C(3B)	1.395(7)	Sn–C(1A)–C(2A)	120.0(3)
C(3B)–C(4B)	1.370(11)	Sn–C(1A)–C(6A)	123.6(3)
C(4B)–C(5B)	1.374(11)	C(2A)–C(1A)–C(6A)	116.0(5)
C(5B)–C(6B)	1.392(7)	C(1A)–C(2A)–C(3A)	122.6(4)
C(1C)–C(2C)	1.408(17)	C(2A)–C(3A)–C(4A)	122.6(4)
C(1C)–C(6C)	1.413(5)	C(3A)–C(4A)–C(5A)	114.8(6)
C(2C)–C(3C)	1.378(21)	C(4A)–C(5A)–C(6A)	122.3(4)
C(3C)–C(4C)	1.384(10)	C(1A)–C(6A)–C(5A)	121.6(4)
C(4C)–C(5C)	1.345(21)	Sn–C(1B)–C(2B)	123.0(4)
C(5C)–C(6C)	1.381(18)	Sn–C(1B)–C(6B)	118.9(4)
		C(2B)–C(1B)–C(6B)	118.1(4)
		C(1B)–C(2B)–C(3B)	120.6(6)
		C(2B)–C(3B)–C(4B)	120.3(6)
		C(3B)–C(4B)–C(5B)	119.8(5)
		C(4B)–C(5B)–C(6B)	120.0(6)
		C(1B)–C(6B)–C(5B)	121.2(5)
		Sn–C(1C)–C(2C)	122.8(4)
		Sn–C(1C)–C(6C)	122.2(7)
		C(2C)–C(1C)–C(6C)	114.9(8)
		C(1C)–C(2C)–C(3C)	122.6(7)
		C(2C)–C(3C)–C(4C)	119.2(14)
		C(3C)–C(4C)–C(5C)	120.7(14)
		C(4C)–C(5C)–C(6C)	120.4(7)
		C(1C)–C(6C)–C(5C)	122.1(9)

Results

The tin(IV) atom is found to be five-coordinate, being bound to three phenyl groups, the nitrogen atom of the isothiocyanato group and an oxygen from the picolinic acid. The geometry around the tin atom is that of a trigonal bipyramid, with the three phenyl groups occupying the equatorial positions, and with the apical sites taken by the nitrogen of the isothiocyanato group and a carboxyl oxygen from the picolinic acid. The acidic proton of picolinic acid has shifted position in the complex, and is bound to the heterocyclic nitrogen atom (the N–H bond length, which is not given in Table II, is 1.17 ± 0.08 Å). The acid is thus coordinated in the form of a zwitterion.

These asymmetric trigonal bipyramidal units are linked together as dimers around centres of symmetry by pairs of water molecules, each of which hydrogen-bonds to the non-coordinated carboxylate oxygen

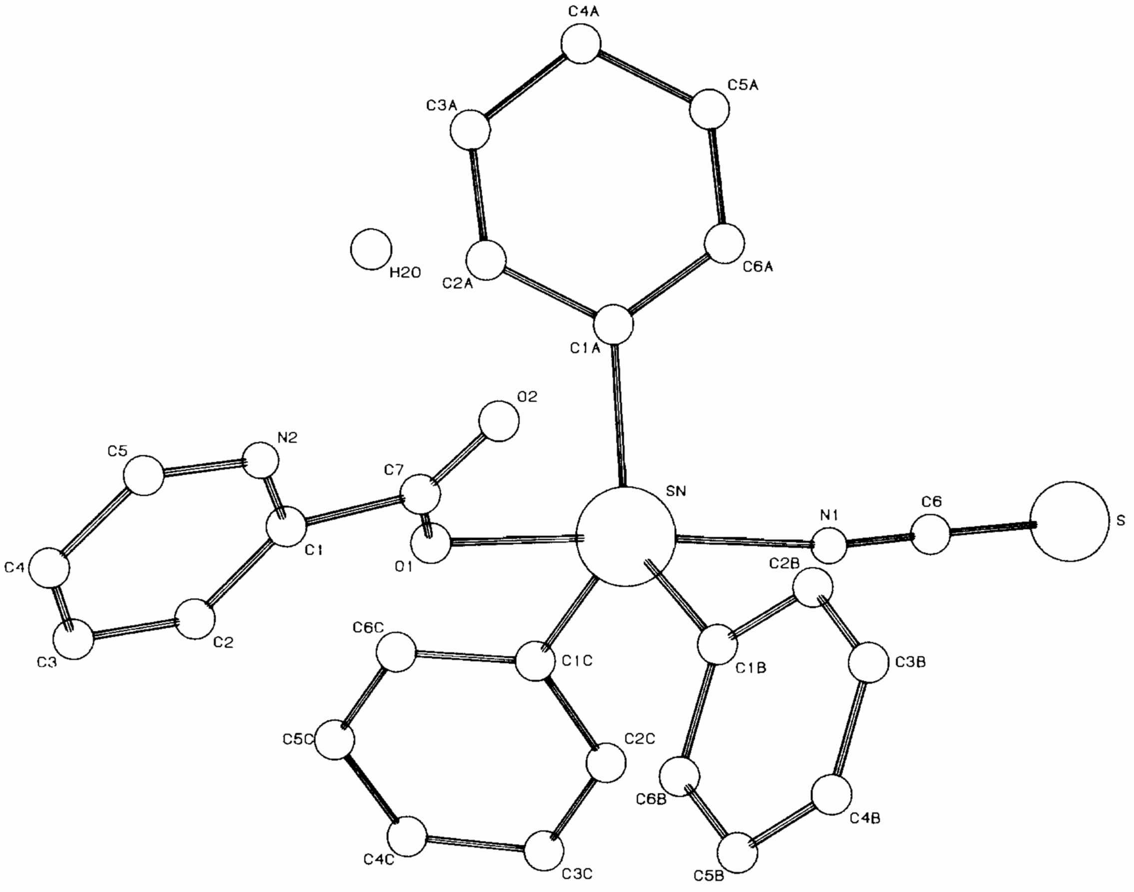

Fig. 1. Molecular configuration and atomic numbering scheme.

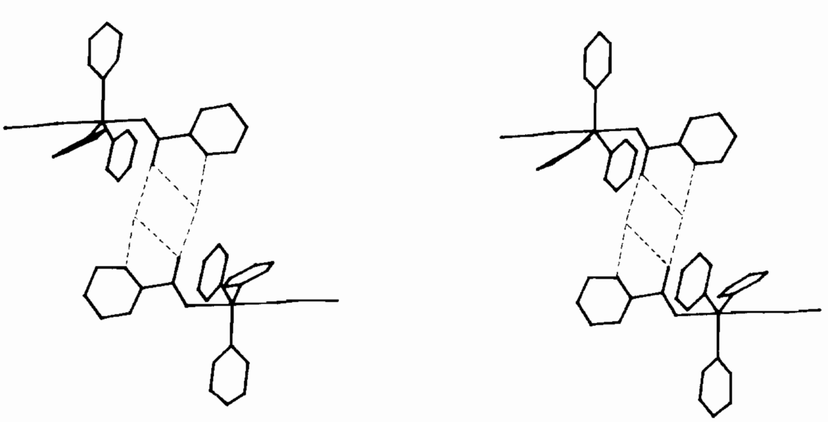

Fig. 2. A stereoview of the dimer showing the hydrogen bonding scheme.

atoms of both picolinic acid molecules, plus the heterocyclic nitrogen atom of one picolinic acid (each water molecule hydrogen-bonding to the heterocyclic nitrogen atom of a different picolinic acid molecule within the dimeric unit). The short contacts between the water molecules and complex monomers are: H_2O to O2 (or O2′, for the other water molecule), 3.246(9) Å; to O2′ (or O2), 2.801(9) Å; and to N2, 2.667(9) Å.

The final atomic positional parameters and the equivalent isotropic temperature factors are given in Table I. The structure of the complex and atomic numbering scheme are shown in Fig. 1, while Table II lists the bond distances and angles. A stereoscopic view of the hydrogen-bonded dimers is given in Fig. 2. The anisotropic thermal parameters and final structure factors have been deposited as supplementary material, and are available from the Editor-in-Chief.

Discussion

The fact that a water molecule is included in the molecular formula of the title compound had led us to suspect that this complex might represent a further example of outer-sphere coordination, in which the ligand is not directly bound to the tin at all but is, instead, held in position by hydrogen-bonding to a coordinated water molecule, as recently reported for a range of triphenyltin species [1, 7–10]. But this turned out not to be the case. The structure of the title compound as described above, is very similar to the structures of the complexes of quinaldic acid [3] and picolinic acid [2] with triphenyltin chloride.

The average Sn–C(Ph) distance of 2.114 Å is somewhat shorter than that found in the analogous chloride complex [2] (2.135 Å), or the quinaldic acid complex [3] of triphenyltin chloride (2.141 Å), but still within the range (2.105–2.16 Å) of Sn–C(Ph) distances reported in the literature [11]. The C–C bond lengths in the phenyl groups are all normal

The NCS group is virtually linear, the NCS angle being 178°. The Sn–N distance of 2.28 Å is exactly the same as that found in the seven-coordinate complex diisothiocyanatodimethyl(terpyridyl)-tin(IV) [12]. The C–S bond length of 1.610 Å and the N–C bond length of 1.155 Å are similar to the bond lengths found in other metal isothiocyanato complexes [13–15].

The Sn–O distance of 2.221 Å is comparable to the Sn–O distance of 2.25 Å found both in dichlorodimethylbis(pyridine N-oxide)tin(IV) [16], and also in aquaisothiocyanatotriphenyl(2,2′:6′,2″-terpyridyl)-tin(IV) [8].

Many organotin complexes of carboxylic acids have been reported [17–21], but these almost always seem to involve bond formation between the organotin moiety and the deprotonated forms of the various acids. The coordination of the protonated form of the acid, in the zwitterion configuration, is most unusual, and seems to have been previously reported only for the triphenyltin chloride complexes of picolinic and quinaldic acids [2, 3].

For the complexes of the deprotonated carboxylic acids, both oxygen atoms of the carboxylate group may coordinate to tin in organotin(IV) species. On the other hand, for the compounds containing protonated carboxylic acids, interaction with the tin appears to be limited to just one of the carboxylate oxygens. In the present case, for example, the Sn–O2 distance is 3.31 Å, which is well outside the normal range of Sn–O bond lengths normally encountered in organotin compounds [22], and is far longer even than the weaker of the two Sn–O bonds (2.65 Å) in tribenzyltin acetate [23] (which has a polymeric structure). We have therefore discounted the possibility of any coordinative interaction between the Sn and O2 atoms.

The isolation of the title compound reinforces our previous finding, that only those acids with a carboxyl group that is *alpha* to the heterocyclic nitrogen atom, are able to form complexes in the protonated form with triphenyltin halide or pseudohalide species. Thus, we have been unable to prepare such complexes with nicotinic or isonicotinic acids and Ph_3SnCl or Ph_3SnNCS.

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