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Chlorotriphenyl(quinolinium-2-carboxylato)tin(IV) Monohydrate*

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Abstract

The crystal structure of chlorotriphenyl(quinolinium-2-carboxylato)tin(IV) monohydrate is reported. The crystals are monoclinic, space group $C2/c$ with cell parameters $a = 20.048(3)$ Å, $b = 11.724(1)$ Å, $c = 23.291(3)$ Å, $\beta = 113.42(1)^\circ$, $Z = 8$, refined to $R_F = 0.034$ on 3331 observed reflections. The tin(IV) atom is five-coordinate, being bound to three phenyl groups, the chlorine atom and an oxygen from the quinaldic acid. The geometry around the tin atom is trigonal bipyramidal, with the three phenyl groups occupying the equatorial positions, and the chlorine and quinaldic acid oxygen, the apical ones. The acidic proton of quinaldic 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 quinaldic acid molecules, plus the heterocyclic nitrogen atom of one quinaldic acid molecule. For complex formation with the protonated acid, the heterocyclic nitrogen should be alpha to the carboxylic acid group.

Introduction

Many organotin complexes of carboxylic acids have been synthesised [1–5] but these almost always seem to involve bond formation between the organotin moiety and the deprotonated forms of the various acids. However, the isolation and crystal structure of the complex between triphenyltin chloride and the protonated form of picolinic acid has recently been reported [6]. The acid binds to the triphenyltin chloride in its zwitterion form. This compound, as well as displaying a most unusual structure, has also shown promising fungicidal activity [7], and we have therefore been prompted to attempt the synthesis of a series of analogous complexes between triphenyltin chloride and other protonated carboxylic acids containing heterocyclic nitrogen atoms.

We describe here the synthesis and crystal structure of one such complex, that formed between triphenyltin chloride and quinaldic acid.

Experimental

Preparation of the Complex

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

The 1:1 complex, $Ph_3SnCl\cdot$quinaldic acid$\cdot H_2O$, was obtained as a white crystalline solid in good yield by mixing hot ethanol solutions containing the stoichiometric quantities of triphenyltin chloride and quinaldic acid. The complex crystallised on standing, was filtered off, washed with cold ethanol and then recrystallised from ethanol (m.p. 98–102 °C).

Microanalyses were performed at the National University of Singapore. Analytical data for $Ph_3SnCl\cdot$quinaldic acid$\cdot H_2O$: Calculated for $C_{28}H_{24}NO_3SnCl$ (%): C, 58.32; H, 4.20; N, 2.43. Found (%): C, 58.24; H, 4.07; N, 2.42.

Crystal Data

Monoclinic. Space group $C2/c$, $a = 20.048(3)$ Å, $b = 11.724(1)$ Å, $c = 23.291(3)$ Å, $\beta = 113.42(1)$, $Z = 8$, $D_{calc} = 1.557$ Mg m^{-3}, $\mu = 1.16$ mm^{-1}.

Intensity Data

Intensity data were collected from a $0.2 \times 0.2 \times 0.3$ mm crystal using graphite monochromatised Mo Kα radiation. 4442 reflections with $2\theta \leqslant 50^\circ$ were measured using the $\theta/2\theta$ technique and profile analysis [8]. Of these, 3331 had $I_{net} > 2.5\sigma(I_{net})$. 238

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systematic absences from the *c*-glide were also measured, and only 1 was significant at the same level. Cell parameters were obtained by least squares from the setting angles of 38 reflections with $45^\circ < 2\theta < 50^\circ$ ($\lambda_{\mathrm{MoK}\alpha} = 0.70932$ Å).

Structure Solution and Refinement

The structure was solved by Patterson and heavy-atom methods and refined with full-matrix least squares. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included at calculated positions and refined isotropically. The two hydrogen atoms of the water molecule were located in a difference map, but were not refined. The final agreement indices are $R_F = 0.034$ and $R_W = 0.029$ for the significant reflections and 0.054 and 0.029 for all reflections. The final D-map is featureless except for peaks with maximum density of ±0.65 e Å^{-3} near the tin atom.

All calculations were performed with the NRC VAX system of programs [9]. Literature [10] values of the scattering factors were used.

Results

The tin(IV) atom is found to be five-coordinate, being bound to three phenyl groups, the chlorine atom and an oxygen from the quinaldic acid. The geometry around the tin atom is that of a trigonal bipyramid, with the three phenyl groups occupying the equatorial positions, and the chlorine and quinaldic acid oxygen, the apical ones.

The acidic proton of quinaldic acid has shifted position in the complex, and is bound to the heterocyclic nitrogen atom (the N–H bond length, which is not shown in Fig. 1, is 0.84 ± 0.03 Å). 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 quinaldic acid molecules, plus the heterocyclic nitrogen atom of one quinaldic acid (each water molecule hydrogen-bonding to the heterocyclic nitrogen atom of a different quinaldic acid molecule within the dimeric unit).

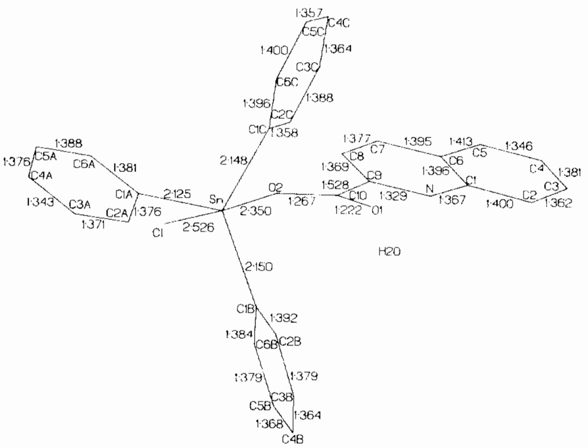

Fig. 1. Atomic numbering scheme and bond lengths (Å) (e.s.d. s are 0.001 Å for the Sn–Cl bond, 0.005 Å for other bonds involving Sn and 0.009–0.011 Å for the remainder).

The final positional and thermal parameters are given in Table I. The atomic numbering scheme and bond lengths are shown in Fig. 1, while Fig. 2 shows the bond angles. A stereoscopic view of the hydrogen-bonded dimers is given in Fig. 3. Tables of the final structure factor listing, the complete distance and angle printout and the complete list of torsion angles are available from the Editor-in-Chief.

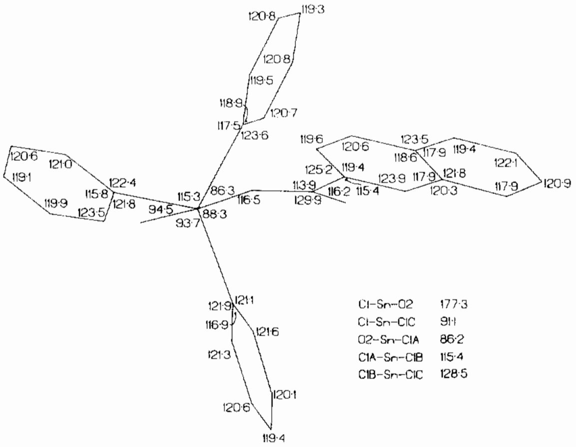

Fig. 2. Bond angles (e.s.d. s from 0.1–0.2° for angles around the Sn atom and 0.5–0.7° for others).

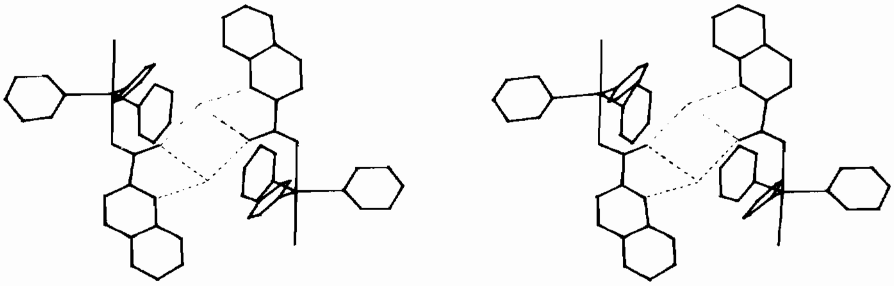

Fig. 3. Stereoscopic view of the hydrogen-bonded dimers.

TABLE I. Positional Parameters and Isotropic Thermal Parameters (e.s.d.s refer to the Last Digit given. For Non-hydrogen Atoms, B_{iso} is the Arithmetic Mean of the Principal Axes of the Thermal Ellipsoid).

	x	y	z	B_{iso}
Sn	0.241071(18)	0.03535(3)	0.137925(15)	3.050(17)
Cl	0.19806(7)	0.07988(11)	0.02269(5)	4.26(8)
N	0.43966(22)	−0.0919(4)	0.37244(18)	3.07(23)
C1	0.4694(3)	−0.1267(4)	0.43348(22)	3.2(3)
C2	0.5449(3)	−0.1345(6)	0.4654(3)	4.7(4)
C3	0.5716(4)	−0.1732(6)	0.5255(3)	5.7(4)
C4	0.5254(4)	−0.2014(6)	0.5543(3)	6.1(4)
C5	0.4527(4)	−0.1928(5)	0.5247(3)	5.0(4)
C6	0.4221(3)	−0.1551(4)	0.46193(22)	3.4(3)
C7	0.3475(3)	−0.1450(4)	0.42719(23)	3.6(3)
C8	0.3210(3)	−0.1083(4)	0.36599(23)	3.1(3)
C9	0.36859(25)	−0.0830(4)	0.33886(20)	2.62(24)
C10	0.3470(3)	−0.0463(4)	0.27090(20)	3.1(3)
O1	0.39457(17)	−0.0513(3)	0.25071(14)	4.39(20)
O2	0.28126(15)	−0.0151(3)	0.24403(12)	3.09(16)
C1A	0.13751(23)	0.0613(4)	0.14078(20)	2.87(23)
C2A	0.1295(3)	0.1225(5)	0.1880(3)	4.1(3)
C3A	0.0635(4)	0.1432(5)	0.1908(3)	5.1(4)
C4A	0.0023(4)	0.1037(7)	0.1455(4)	6.4(5)
C5A	0.0071(3)	0.0409(8)	0.0974(4)	6.6(4)
C6A	0.0740(4)	0.0214(6)	0.0945(3)	5.1(4)
C1B	0.31351(23)	0.1791(4)	0.16599(21)	2.82(23)
C2B	0.3384(3)	0.2217(5)	0.22672(25)	3.8(3)
C3B	0.3807(3)	0.3187(5)	0.2441(3)	4.7(4)
C4B	0.4001(3)	0.3746(5)	0.2017(3)	4.6(3)
C5B	0.3773(3)	0.3335(5)	0.1419(3)	4.0(3)
C6B	0.3336(3)	0.2382(4)	0.12394(24)	3.2(3)
C1C	0.26489(25)	−0.1376(4)	0.12225(21)	2.98(24)
C2C	0.2938(3)	−0.1677(5)	0.0807(3)	3.9(3)
C3C	0.3078(3)	−0.2812(6)	0.0727(3)	4.8(3)
C4C	0.2926(3)	−0.3653(5)	0.1062(3)	4.9(4)
C5C	0.2629(3)	−0.3370(5)	0.1474(3)	4.7(4)
C6C	0.2489(3)	−0.2230(5)	0.15665(24)	3.8(3)
H20	0.4483(3)	−0.0038(7)	0.15906(22)	7.8(4)
H2	0.5746(21)	−0.119(4)	0.4438(18)	3.0(11)
H3	0.619(3)	−0.169(4)	0.5434(23)	5.6(16)
H4	0.540(3)	−0.218(4)	0.5896(21)	4.2(14)
H5	0.4216(24)	−0.206(4)	0.5459(21)	4.6(14)
H7	0.3179(18)	−0.160(3)	0.4481(15)	1.2(8)
H8	0.2732(21)	−0.095(3)	0.3442(18)	3.0(11)
H2A	0.1707(20)	0.150(3)	0.2159(18)	2.6(11)
H3A	0.050(3)	0.189(5)	0.2214(24)	7.2(17)
H4A	−0.047(3)	0.105(5)	0.1454(24)	7.1(17)
H5A	−0.0264(25)	0.010(4)	0.0733(22)	4.8(16)
H6A	0.0779(22)	−0.015(4)	0.0665(17)	2.3(11)
H2B	0.3241(23)	0.189(4)	0.2536(20)	3.6(13)
H3B	0.3896(23)	0.348(4)	0.2798(19)	3.9(13)
H4B	0.4293(22)	0.440(4)	0.2113(19)	4.3(13)
H5B	0.3932(23)	0.366(4)	0.1149(19)	3.8(12)
H6B	0.3161(21)	0.210(3)	0.0811(19)	3.0(11)
H2C	0.3024(24)	−0.118(4)	0.0539(20)	4.7(13)
H3C	0.3337(23)	−0.301(4)	0.050(20)	4.0(13)
H4C	0.2925(22)	−0.440(4)	0.0955(19)	4.0(12)
H5C	0.250(3)	−0.399(4)	0.1720(22)	6.6(15)
H6C	0.2259(24)	−0.202(4)	0.1832(21)	4.8(14)
HN	0.4697(19)	−0.077(3)	0.3566(16)	1.4(10)
HW1	0.4188(19)	−0.019(3)	0.1881(16)	6.3(10)
HW2	0.4876(19)	0.022(3)	0.1688(16)	6.3(10)

Discussion

Quinaldic acid is potentially a bidentate ligand, and when the title compound was first isolated, three possibilities for the structure were envisaged. It was considered that the tin(IV) atom could be six-coordinate, being bound to three phenyl groups and the chlorine atom, along with an oxygen and a nitrogen from the quinaldic acid. Another possibility was that this molecule might represent a further example of outer-sphere coordination, in which the ligand is not directly bound to the tin at all, but rather held in position by hydrogen-bonding to a coordinated water molecule, as recently reported for a range of triphenyltin species [11–15]. The third conceivable structure was the one actually found, in which the tin(IV) atom has a five-coordinate structure involving the coordination of the zwitterion form of the acid. This is the same unusual structure as that displayed by the (protonated) picolinic acid complex of Ph_3SnCl [6].

The average Sn–C(Ph) distance of 2.141 Å is almost the same as that found in the analogous picolinic acid complex (2.135 Å) [6], and within the range (2.105–2.16 Å) of Sn–C(Ph) distances reported in the literature [16]. The C–C bond lengths in the phenyl groups are all normal.

The Sn–Cl distance of 2.526 Å is also very similar to that found [6] in the picolinic acid complex (2.515 Å), and again is within the range of Sn–Cl distances (2.32–2.58 Å) in other chloro complexes [16].

The Sn–O distance of 2.350 Å is virtually the same as that found in the picolinic acid complex (2.347 Å), and longer than the Sn–O distances of 2.25 Å in dichlorodimethylbis(pyridine N-oxide)tin(IV) [17], 2.317 Å in aquachlorotriphenyl(2,2′:6′,2″-terpyridyl)tin(IV) [12] or 2.25 Å in aquaisothiocyanatotriphenyl(2,2′:6′,2″-terpyridyl)tin(IV) [13]. The elongation of the Sn–O distance in the carboxylic acid complexes is probably partially due to the double-bond character of the C–O bonds. We have found 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 chloride. Thus, we were unable to prepare such complexes with nicotinic or isonicotinic acids and Ph_3SnCl.

It would therefore appear that the presence of the *alpha*-nitrogen is essential for the formation of this type of complex, probably to facilitate the proton-transfer process, which is essentially the conversion of the hydrogen bond between the acidic proton and the heterocyclic nitrogen in the free acid, into a covalency in the complex (there now being a hydrogen bond in place of the former covalency).

The contrast in the structure of the title compound with those of the triphenyltin complexes of phenanthroline and bipyridine [11] is most interesting. Both have the same empirical formula, $Ph_3SnCl \cdot L \cdot H_2O$, where L is potentially a planar bidentate, both show a trigonal bipyramidal geometry around the tin atom and both exist as hydrogen-bonded dimers. But, in the title compound, L is coordinated to the tin and the water molecule serves to bind the five-coordinate units together in the dimer. On the other hand, in the phen and bipy complexes, it is the water molecule which is coordinated to the tin atom, and the molecules of phenanthroline or bipyridine which bind the monomeric units into the dimer.

Once again, the reluctance of triorganotin halide complexes to adopt a six-coordinate configuration is amply demonstrated.

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