OUTER-SPHERE COORDINATION OF 1,10-PHENANTHROLINE IN BIS(AQUATRIFLUOROACETATOTRIPHENYLTIN· 1,10-PHENANTHROLINE)

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Triphenyltin chloride and tri(*p*-chlorophenyl)tin chloride both form water-coordinated 1/1 complexes with 1,10-phenanthroline monohydrate in which hydrogen bonds link the heterocyclic base to the aquachlorotriaryltin entities [1,2]. In the crystal structure of the aquachlorotri(*p*-chloro)phenyltin complex, the aqua ligand, which engages in hydrogen bonding with the nitrogen atom of one 1,10-phenanthroline, is also hydrogen bonded to a nitrogen atom of another heterocycle, the interactions resulting in the formation of a dimeric compound. The preference of these Lewis acids to afford "outer-sphere coordination" complexes with the diimine prompted a structural investigation into a claim [3], presented on the basis of spectroscopic measurements, that triphenyltin trifluoroacetate yields an "inner-sphere coordination" complex with this Lewis base.

Experimental

Triphenyltin hydroxide and trifluoroacetic acid (1/1 molar ratio) were dissolved in a small volume of hot ethanol and an equimolar quantity of 1,10-phenanthroline monohydrate was then added. Slow cooling of the filtered solution gave large crystals of the title complex.

Diffraction measurements were carried out on an Enraf-Nonius CAD4 diffractometer (Mo-$K\alpha$, 0.71073 Å) up to $2\theta = 50°$ [4] (collection range: $-9 < h < 9$, $-14 < k < 14$, $0 < l \leq 14$). The 4936 raw intensities were reduced by the *NRCVAX* [5] program for solution by *SHELXS-86* [6] and refinement by *SHELXL-93* [7]. An absorption correction [8] (transmission factors = 0.637 - 1.000) was applied to the model. H-atoms were generated and were allowed to ride on their parent C-atoms with $U(\mathrm{H}) = 1.5U_{eq}(\mathrm{C})$. One of the two H-atoms of the water molecule was located whereas the other was generated geometrically. The refinement on F^2 for 382 parameters converged (shift-to-error ≤ 0.001) to $R = 0.0710$ and $S = 1.088$ for all data; $R_1 = 0.0416$ for 3521 $I \geq 2\sigma(I)$ reflections. Atomic coordinates are listed in Table 1.

Crystal data: $C_{32}H_{25}F_3N_2O_3Sn$, $FW = 661.23$, triclinic, $P1$, $a = 9.5756(7)$, $b = 12.217(1)$, $c = 12.6178(6)$ Å, $\alpha = 91.174(6)$, $\beta = 98.169(5)$, $\gamma = 90.493(6)$1)°.1)°.$V = 1460.7(2)$ Å^3, $D_{calc} = 1.503$ Mg m^{-3}, $\mu = 0.929$ mm^{-1}, $F(000) = 664$ for $Z = 2$.

Table 1. Atomic coordinates and equivalent[a] isotropic displacement parameters for bis(aquatrifluoroacetatotriphenyltin·1,10-phenanthroline)

Atom	x	y	z	U_{eq}
Sn(1)	0.1604(1)	0.2201(1)	0.3156(1)	0.049(1)
O(1)	0.2588(5)	0.3291(3)	0.2088(4)	0.065(1)
O(2)	0.2414(6)	0.4892(4)	0.2929(4)	0.083(1)
O(3)	0.0577(4)	0.0977(3)	0.4225(3)	0.054(1)
N(1)	-0.2202(5)	0.0359(4)	0.3393(4)	0.057(1)
N(2)	-0.0673(6)	-0.1528(4)	0.3589(4)	0.058(1)
F(1)[b]	0.391(1)	0.4404(8)	0.0684(8)	0.136(4)
F(2)[b]	0.173(2)	0.483(2)	0.045(1)	0.206(8)
F(3)[b]	0.333(2)	0.5887(8)	0.1352(9)	0.175(6)
F(1')[c]	0.243(3)	0.454(2)	0.035(2)	0.123(8)
F(2')[c]	0.229(3)	0.585(2)	0.110(2)	0.135(9)
F(3')[c]	0.429(3)	0.511(3)	0.130(2)	0.173(9)
C(1)	0.1661(6)	0.0897(4)	0.2009(4)	0.047(1)
C(2)	0.1753(6)	-0.0181(5)	0.2330(5)	0.059(2)
C(3)	0.1830(7)	-0.1030(5)	0.1579(6)	0.067(2)
C(4)	0.1819(6)	-0.0788(6)	0.0523(5)	0.067(2)
C(5)	0.1710(7)	0.0280(6)	0.0193(5)	0.068(2)
C(6)	0.1648(6)	0.1121(5)	0.0934(5)	0.055(1)
C(7)	-0.0263(7)	0.3164(4)	0.3038(5)	0.057(2)
C(8)	-0.1176(8)	0.3209(6)	0.2090(6)	0.080(2)
C(9)	-0.242(1)	0.3789(8)	0.2064(9)	0.106(3)
C(10)	-0.275(1)	0.4307(8)	0.294(1)	0.110(3)
C(11)	-0.184(1)	0.4297(7)	0.3881(9)	0.101(3)
C(12)	-0.0595(8)	0.3738(6)	0.3935(6)	0.073(2)
C(13)	0.3274(6)	0.2354(4)	0.4447(5)	0.054(1)
C(14)	0.3853(6)	0.1437(5)	0.4956(5)	0.060(2)
C(15)	0.4975(7)	0.1509(6)	0.5769(6)	0.074(2)
C(16)	0.5550(8)	0.2513(8)	0.6097(6)	0.085(2)
C(17)	0.5002(9)	0.3423(7)	0.5611(7)	0.095(3)
C(18)	0.3874(8)	0.3358(6)	0.4791(6)	0.077(2)
C(19)	0.2603(7)	0.4307(6)	0.2172(5)	0.063(2)
C(20)	0.296(1)	0.4882(7)	0.1177(7)	0.100(3)
C(21)	-0.2632(6)	-0.0502(5)	0.2732(4)	0.052(1)
C(22)	-0.3009(7)	0.1234(6)	0.3324(6)	0.071(2)
C(23)	-0.4248(8)	0.1322(7)	0.2604(8)	0.088(2)
C(24)	-0.4646(8)	0.0471(8)	0.1923(7)	0.087(2)
C(25)	-0.3869(7)	-0.0471(6)	0.1965(5)	0.068(2)
C(26)	-0.423(1)	-0.1407(9)	0.1272(6)	0.095(3)
C(27)	-0.341(1)	-0.2283(8)	0.1319(6)	0.093(3)
C(28)	-0.2157(9)	-0.2358(6)	0.2071(6)	0.075(2)
C(29)	-0.127(1)	-0.3250(6)	0.2126(7)	0.095(3)
C(30)	-0.011(1)	-0.3272(6)	0.2864(8)	0.097(3)
C(31)	0.0137(8)	-0.2388(6)	0.3605(6)	0.079(2)
C(32)	-0.1793(6)	-0.1473(5)	0.2809(4)	0.053(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Atom refined with 2/3 site occupancy.

[c] Atom refined isotropically with 1/3 site occupancy.

Results and discussion

Triphenyltin trifluoroacetate reacts with 1,10-phenanthroline to give a five-coordinate water-coordinated complex (Fig. 1) instead of the six-coordinate *N,N*-chelated complex that has been predicted from spectroscopic data. The trifluoroacetato anion is unidentate, the carboxyl oxygen atom occupying one apical site of the trigonal bipyramid (ΣC-Sn-C = 359.6(6)°) around the tin atom. The water molecule occupies the other apical position, and is hydrogen bonded to the nitrogen atom of one 1,10-phenanthroline unit (O···N = 2.809(6) Å) and also to the nitrogen atom of a centrosymmetrically-related unit (O···N = 2.814(6) Å) (Fig. 2). The hydrogen bonding interactions give rise to the formation of a dimeric entity. The two heterocycles are held half-way between the aqua ligands, and the plane of the heterocycle is approximately perpendicular to the water-water axis. The structure of this dimer is similar to that of the dimeric aquatri(*p*-chlorophenyl)tin complex, and bond dimensions involving the central metal atom in the two structures do not differ significantly. The aquatri(*p*-chlorophenyl)tin complex consists of two symmetry-independent monomers [2], and the dimers are packed in the unit cell in such a manner that chlorine-chlorine repulsions are minimized.

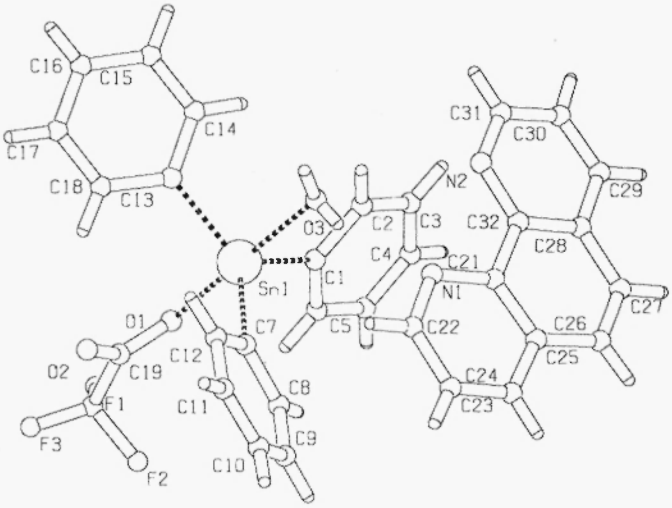

Fig. 1. *PLUTON* [9] plot of aquatrifluoroacetatotriphenyltin 1,10-phenanthroline monomer. Selected bond distances and angles: Sn(1)-C(1) = 2.136(5), Sn(1)-C(7) = 2.138(6), Sn(1)-C(13) = 2.118(6), Sn(1)-O(1) = 2.213(4), Sn(1)-O(3) = 2.335(4) Å; C(1)-Sn(1)-C(7) = 117,6(2), C(1)-Sn(1)-C(13) = 118.7(2), C(1)-Sn(1)-O(1) = 88.9(2), C(1)-Sn(1)-O(3) = 88.3(2), C(7)-Sn(1)-C(13) = 123.3(2), C(7)-Sn(1)-O(1) = 92.3(2), C(7)-Sn(1)-O(3) = 89.2(2), C(13)-Sn(1)-O(1) = 95.0(2), C(13)-Sn(1)-O(3) = 86.2(2), O(1)-Sn(1)-O(3) = 177.1(1)°.

The crystal structure of triphenyltin trifluoroacetate itself has not been reported, but Mössbauer and infrared measurements [10] implicate a five-coordinate carboxylate-bridged structure, a conformation commonly adopted by triphenyltin alkanoates [11]. Carboxylate bridging in this compound is relinquished in favor of hydrate formation in the 1,10-phenanthroline complex, which is stabilized by hydrogen bonding to two heterocycles.

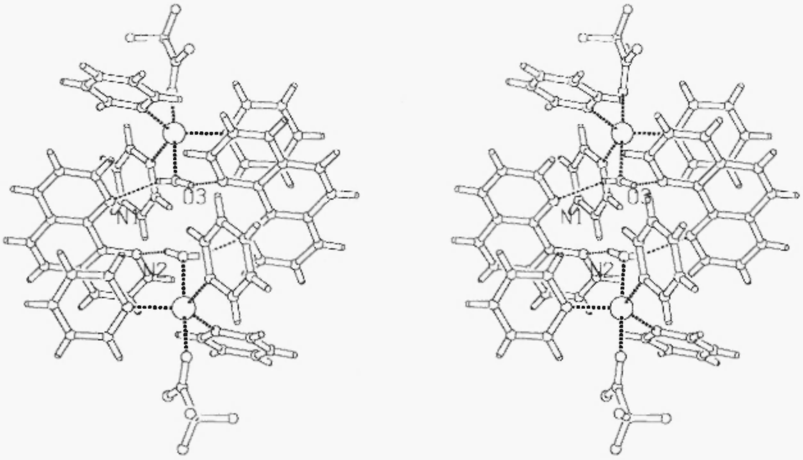

Fig. 2. Stereoview of bis(aquatrifluoroacetatotriphenyltin·1,10-phenanthroline). Hydrogen bonds: O(3)···N(1) = 2.809(6), O(3)···N(2)' = 2.814(6) Å, N(1)···O(3)···N(2)' = 111.4(2)°. Symmetry transformation ('): *-x*, *-y*, 1 - *z*.

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