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Solid-state ^{119}Sn NMR and Antitumor Activity of Bis [1,3-Bis (3-oxapentamethylene-carbamoylthioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxare], and the Crystal Structure of its Bis-ethanol Solvate

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The ^{119}Sn cross polarization-magic angle spinning NMR spectrum of bis[1,3-bis(3-oxapentamethylenecarbamoylthioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxane], $\{[(C_4H_9)_2SnO_2CCH_2SC(O)N(CH_2CH_2)_2O]_2O\}_2$, which consists of two resonances of similar chemical shifts and symmetry ($\delta_{iso} = -152$, -202 ppm; asymmetry, $\kappa = 0.38$), implies the existence of two five-coordinate tin sites in the centrosymmetric dimer. The assignment has been corroborated by X-ray diffraction analysis on the compound that has been crystallized from ethanol; the crystal structure shows two tin atoms in *cis*-C_2SnO_3 trigonal-bipyramidal coordination [C-Sn-C = 131.5(1), 131.3(2) °]. The analysis also reveals the presence of two lattice ethanol molecules that are hydrogen-bonded to the dimer [O···O = 2.779(5) Å]. When exposed to air, the distannoxane loses ethanol. The unsolvated distannoxane is more active than *cis*-platin when screened against MCF-7 (mammary cancer), EVSA-T (mammary cancer), WiDr (colon cancer), IGROV (ovarian cancer), M19 MEL (melanoma), A498 (renal cancer) and H226 (lung cancer) cell lines.

Keywords: tetrabutyldistannoxane; solid-state NMR; crystal structure; antitumor activity

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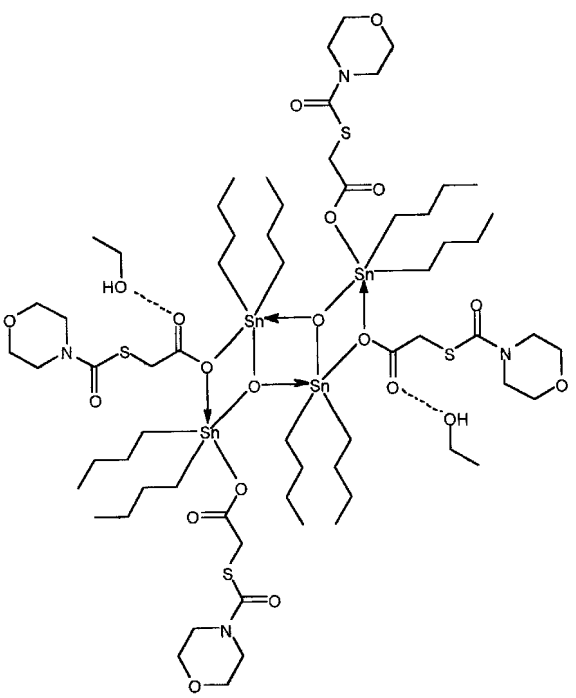
INTRODUCTION

The 1,1,3,3-tetrabutyldi(carboxylato)distannoxanes, $\{[(C_4H_9)_2SnO_2CR]_2O\}_2$, which are the products of condensation between dibutyltin oxide and a monobasic carboxylic acid, crystallize as centrosymmetric dimers having a characteristic central $Sn_{endocyclic}$–$O_{endocyclic}$–$Sn'_{endocyclic}$–$O'_{endocyclic}$ core flanked on opposite sides by $Sn_{endocyclic}$–$O_{endocyclic}$–$Sn_{exocyclic}$–$O_{exocyclic}$ and $Sn'_{endocyclic}$–$O'_{endocyclic}$–



Scheme 1

 CCC 0268–2605/2000/010001–07 $17.50

$Sn'_{exocyclic}$–$O'_{exocyclic}$ rings.[1] In antitumor investigations *in vitro* of these compounds against MCF-7 (mammary cancer) and WiDr (colon cancer) cell lines, the R = 2,3,4-$(OCH_3)_3C_6H_2$— is the most active derivative in the substituted-phenyl series and the R = 4-(NH_2)-2-$(OH)C_6H_3$ is the most active derivative in the salicyl series,[2] the activities of these two compounds exceeding that of *cis*-platin.[3] Such high activity implicates the contribution of the anionic moiety to the overall antitumor activity of the organotin compound. On the other hand, as a fungitoxicity investigation on the triorganotin derivatives of carbamoyl-substituted acetic acids has similarly confirmed the contribution of the anionic group to the overall biological activity of these carboxylates,[4] the antitumor activity of the tetrabutyldistannoxanes can be expected to be similarly enhanced by the use of a carbamoylthioacetato unit as the carboxylato anion. The antitumor activity of bis[1,3-bis(3-oxapentamethylenecarbamoylthioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxane] against several cancer cell lines is described in this report, which also details its solid-state NMR and 119*m*–Sn Mössbauer spectral parameters. The compound has also been characterized by X-ray crystallography as the bis-ethanol solvate (Scheme 1).

EXPERIMENTAL

Synthesis

The carboxylic acid $[O(CH_2CH_2)_2NC(O)SCH_2CO_2H]$ was synthesized from morpholine, carbonyl sulfide and chloroacetic acid by a modification of the method[5] for preparing *N*,*N*-dimethylcarbamoylthioacetic acid. Equimolar quantities of the carbamoylthioacetic acid and dibutyltin oxide were heated in several drops of ethanol until the oxide had dissolved completely. The solution, when cool, solidified to a faint-tan material. The compound was dissolved in a small volume of ethanol; slow cooling of the filtered solution yielded large transparent blocks. The crystals could be taken out of the ethanol solution and are stable in the air for several hours, but will turn opaque overnight. The reaction with 2:1 acid/oxide stoichiometry gave only the distannoxane. Elemental analysis for opaque $\{[(C_4H_9)_2SnO_2CCH_2SC(O)N(CH_2CH_2)_2O]_2\}_2$: Found: C 40.61, H 6.40, N 2.94; Calcd for $C_{60}H_{112}N_4O_{18}S_4Sn_4$: C 40.47, H 6.34, N 3.15%. The 119*m*–Sn Mössbauer spectrum at 77 K showed only one quadropole-split doublet: isomer shift = 1.31, quadrupole splitting = 3.20, $\Gamma_1 = 0.98$, $\Gamma_2 = 1.00$ mm s^{-}.

NMR

Solid-state ^{119}Sn (111.922 MHz) and ^{13}C (75.47 MHz) NMR spectra were recorded on a Bruker MSL-300S instrument.[6] The ^{119}Sn NMR spectra, which were acquired at 8 kHz, were analyzed by using Bruker's WINFIT to derive the principal components of the chemical shift tensor. The components are defined as: $\delta_{11} > \delta_{22} > \delta_{33}$; isotropic chemical shift, $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$; span, $\omega = \delta_{11} - \delta_{33}$; skew, $\kappa = 3(\delta_{22} - \delta_{iso})/\omega$; anisotropy, $\Delta = \delta_{33} - \delta_{iso}$; asymmetry, $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})$.[7] Site 1: $\delta_{iso} - 152$ ppm; ($\delta_{11} = 269$, $\delta_{22} = -29$, $\delta_{33} = -696$); $\omega = -965$; $\kappa = 0.38$; $\Delta = -543$ ppm; $\eta = 0.55$. Site 2: $\delta_{iso} = -202$ ppm; ($\delta_{11} = 252$, $\delta_{22} = -70$, $\delta_{33} = -788$); $\omega = -1040$; $\kappa = 0.38$; $\Delta = -586$ ppm; $\eta = 0.55$. ^{13}C NMR: δ_C 176.4, 172.5 (—CO_2), 166.9 (—COS), 65.9 (O—CH_2—), 45.1 (N—CH_2—); 42.2 (S—CH_2—); 35–20 (multiplet, —CH_2— of butyl groups), 14.8, 13.1 (—CH_3). The cross polarization-magic angle spinning ^{119}Sn NMR is shown in Fig. 1.

Crystal Structure

For the room-temperature diffraction measurements, a crystal of **1** was removed from the mother liquor and cut into an approximately 0.3 mm × 0.3 mm × 0.3 mm specimen, which was immediately coated with epoxy glue. Auto-indexing procedures on the CAD-4 diffractometer (graphite-monochromatized Mo–$K\alpha$ radiation, $\lambda = 0.71073$ Å)[8] gave a triclinic cell, and the unit cell was refined from 25 reflections in the $14° \leq \theta \leq 16°$ shell. The 12 639 reflections were measured by ω-scans to $2\theta = 60°$ (collection range: $0 \leq h \leq 17$, $-18 \leq k \leq 17$, $-19 \leq l \leq 19$), and were corrected for absorption[9] and decay. The raw intensities were reduced to F^2 and $\sigma(F^2)$ values[10] for solution[11] and refinement.[12] The refinement on 12 105 independent reflections converged with a shift-to-error ratio of less than 0.001 to a final R index of 0.0361 for the 8929 $I > 2\sigma(I)$ reflections. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated and allowed to ride on their parent atoms with $U = 1.5\ U_{eq}$(C); the hydroxyl H-atom was located and refined. The final difference map had peaks between −0.475 and 0.566 e Å^{-3} only. The C_2 atom of one of the butyl chains is disordered over

Table 1 Atomic coordinates and equivalent isotropic temperature factors ($Å^2$) for bis[1,3-bis(3-oxapentamethyl-enecarbamoylthioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxane] bis-ethanol solvate

Atom	*x*	*y*	*z*	U_{eq} [a]
Sn1a	0.06977(2)	0.12151(1)	0.46561(1)	0.03803(6)
S1a	0.50632(7)	0.30155(8)	0.30576(7)	0.0624(2)
O1a	0.2513(2)	0.1287(2)	0.4404(2)	0.048(1)
O2a	0.2822(2)	0.2948(2)	0.3975(2)	0.069(1)
O3a	0.3317(3)	0.1772(2)	0.1944(2)	0.086(1)
O4a	0.5516(4)	0.3670(3)	−0.0589(2)	0.109(1)
N1a	0.4541(3)	0.3075(3)	0.1170(2)	0.079(1)
C1a	0.1033(3)	0.2347(3)	0.5858(3)	0.081(1)
C2a (82.5%)	0.2118(4)	0.2663(5)	0.6420(4)	0.091(2)
C2′ (17.5%)	0.175(2)	0.3437(8)	0.6033(8)	0.053(5)
C3a	0.2315(5)	0.3701(4)	0.7085(3)	0.106(2)
C4a	0.1502(6)	0.3628(5)	0.7857(4)	0.129(2)
C5a	0.0244(3)	0.1343(3)	0.3154(2)	0.054(1)
C6a	−0.0244(4)	0.0287(3)	0.2580(2)	0.067(1)
C7a	−0.0577(4)	0.0417(4)	0.1507(3)	0.083(1)
C8a	−0.1166(5)	−0.0618(4)	0.0954(3)	0.117(2)
C9a	0.3141(2)	0.2150(2)	0.4068(2)	0.046(1)
C10a	0.4314(3)	0.2055(3)	0.3848(3)	0.058(1)
C11a	0.4184(3)	0.2540(3)	0.1962(3)	0.063(1)
C12a	0.3859(5)	0.2831(5)	0.0231(3)	0.105(2)
C13a	0.4610(6)	0.2744(5)	−0.0565(4)	0.115(2)
C14a	0.6200(5)	0.3835(4)	0.0310(3)	0.101(2)
C15a	0.5547(4)	0.3982(3)	0.1157(3)	0.086(1)
Sn1a	0.24131(2)	−0.05862(2)	0.47911(1)	0.04126(6)
S1b	0.04701(8)	−0.41841(8)	0.61118(7)	0.0626(2)
O1b	0.1499(2)	−0.2091(2)	0.5252(2)	0.050(1)
O2b	0.3203(2)	−0.2299(2)	0.5071(2)	0.057(1)
O3b	0.1928(2)	−0.3222(3)	0.7580(2)	0.084(1)
O4a	−0.1523(3)	−0.4213(3)	0.9385(2)	0.108(1)
N1b	0.0104(3)	−0.3904(3)	0.7983(2)	0.066(1)
C1b	0.2679(3)	−0.0872(3)	0.3297(2)	0.057(1)
C2b	0.1958(4)	−0.1878(3)	0.2780(3)	0.076(1)
C3b	0.2276(6)	−0.2074(4)	0.1733(3)	0.110(2)
C4b	0.2203(7)	−0.1294(6)	0.1066(4)	0.154(3)
C5b	0.3573(3)	0.0097(3)	0.6014(2)	0.060(1)
C6b	0.3397(3)	−0.0499(3)	0.6939(3)	0.066(1)
C7b	0.4164(4)	0.0013(4)	0.7799(3)	0.092(1)
C8b	0.3992(5)	−0.0576(5)	0.8718(3)	0.112(2)
C9b	0.2216(3)	−0.2663(2)	0.5293(2)	0.045(1)
C10b	0.1832(3)	−0.3786(3)	0.5589(3)	0.060(1)
C11b	0.0930(3)	−0.3705(3)	0.7348(3)	0.061(1)
C12b	0.0445(4)	−0.3685(4)	0.9029(3)	0.094(2)
C13b	−0.0490(5)	−0.3419(5)	0.9554(4)	0.111(2)
C14b	−0.1871(4)	−0.4308(5)	0.8373(4)	0.108(2)
C15b	−0.1021(4)	−0.4634(4)	0.7761(3)	0.088(1)
O1	0.0917(2)	−0.0253(2)	0.4947(1)	0.042(1)
O2	0.3252(4)	0.5138(3)	0.3814(4)	0.140(2)
C1	0.4412(6)	0.5730(5)	0.3891(6)	0.141(3)
C2	0.4557(6)	0.6656(5)	0.3313(5)	0.130(2)

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

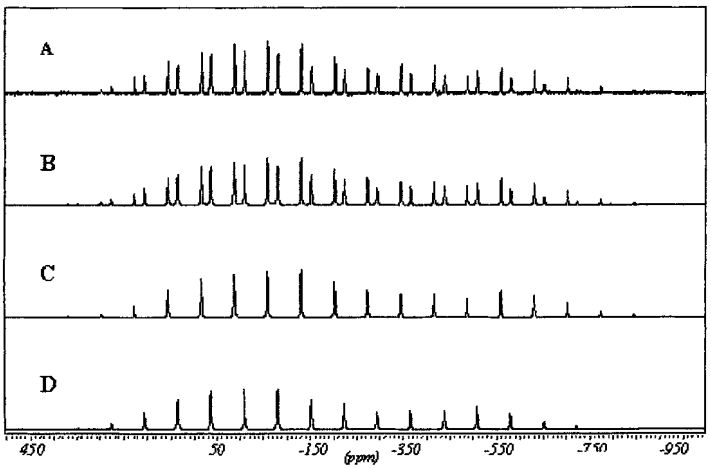


Figure 1 Solid-state CP–MAS ^{119}Sn spectra of bis[1,3-bis(3-oxapentamethylenecarbamoyl-thioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxane] recorded at 8 kHz: (A) experimental spectrum; (B) sum [(C) + (D)] of the simulated spectra; (C) simulation of site 2, δ_{iso} −202 ppm; (D) simulation of site 1, δ_{iso} −152 ppm.

two positons; this butyl chain was subjected to a 1,2-related C–C distance restraint of 1.54 ± 0.01 Å. Atomic coordinates and equivalent isotropic temperature factors are presented in Table 1; the structure is depicted as an ORTEP[13] plot in Fig. 2. Tables of bond lengths, bond angles and anisotropic temperature factors are deposited at the Cambridge Crystallographic Database Centre.[14]

In vitro antitumor activity

The unsolvated distannoxane (**1**) was screened against MCF-7 (mammary cancer), EVSA-T (mammary cancer), WiDr (colon cancer), IGROV (ovarian cancer), M19 (melanoma), MEL A498 (renal cancer) and H226 (lung cancer) cell lines by using an *in vitro* method.[15] The inhibition dosages (ID_{50}) in water/ethanol (99:1) and those of reference compounds are presented in Table 2.

RESULTS AND DISCUSSION

NMR

The solid-state CP–MAS ^{119}Sn NMR spectrum (Fig. 1) of the unsolvated distannoxane shows two tin sites of similar chemical shift and symmetry. Site 1 has an isotropic chemical shift of δ_{iso} =

Table 2 ID_{50} values of bis[1,3-bis(3-oxapentamethylenecarbamoylthioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxane] (**1**) and of other reference drugs[a]

Compound	MCF-7	EVSA-T	WiDr	IGROV	M19 MEL	A498	H226
Distannoxane (**1**)	41	48	125	63	78	96	92
Cis-platin	699	422	967	169	558	2253	3269
Doxorubicin	10	8	11	60	16	90	199
Etoposide	2594	317	150	580	505	1314	3934
5-Fluorouracil	750	475	225	297	442	143	340
Methotrexate	18	5	<3	7	23	37	2287

[a] Data from Ref. 15

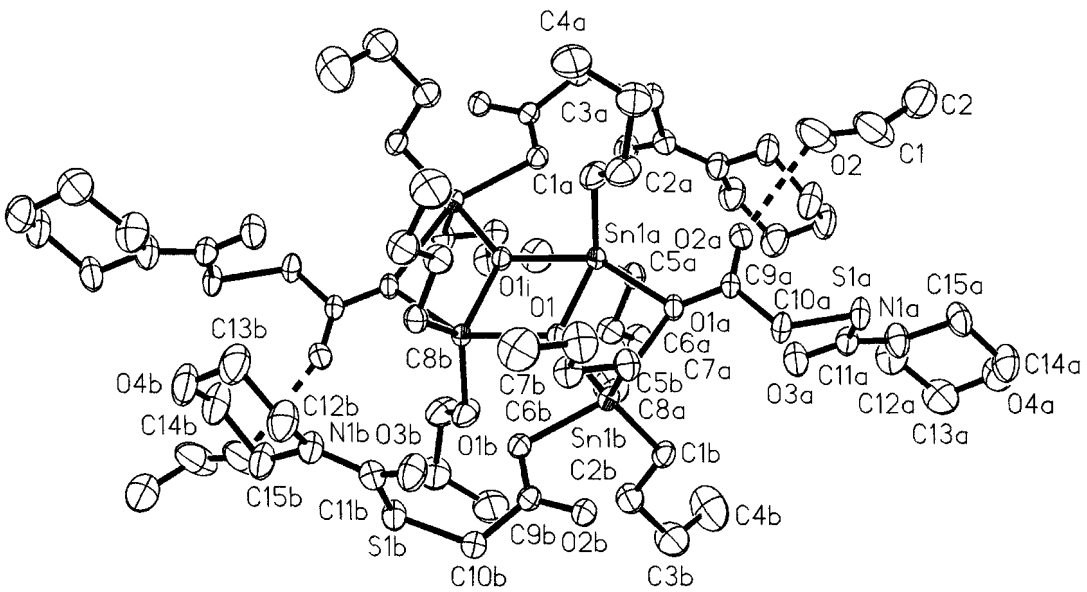


Figure 2 ORTEP plot of bis[1,3-bis(3-oxapentamethylenecarbamoylthioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxane] bis-ethanol solvate at the 25% probability level; hydrogen atoms are not shown. Selected bond distances (Å) and angles (deg.): Sn1a–C1a 2.111(4), Sn1a–C5a 2.118(3), Sn1a–O1a 2.238(2), Sn1a–O1 2.049(2), Sn1a–O1^{i} 2.147(2), Sn1a···O1a^{i} 3.183(2), Sn1a–C1b 2.122(3), Sn1b–C5b 2.125(3), Sn1b–O1a 2.487(2), Sn1b–O1b 2.119(2), Sn1b–O1 2.004(2), Sn1b···O2b 2.684(2) Å C1a–Sn1a–C5a 131.3(2), C1a–Sn1a–O1a 97.3(1), Cla–Sn1a–O1 115.9(2), C1a–Sn1a–O1^{i} 97.9(1), C5a–Sn1a–O1a 93.7(1), C5a–Sn1a–O1 112.8(1), C5a–Sn1a–O1^{i} 98.4(1), O1a–Sn1a–O1 73.32(7), O1a–Sn1a–O1^{i} 146.5(1), O1–Sn1a–O1^{i} 73.2(1), C1b–Sn1b–C5b 131.5(1), C1b–Sn1a–O1a 87.6(1), C1b–Sn1b–O1b 104.9(1), C1b–Sn1a–O1 112.1(1), C5a–Sn1a–O1a 85.6(1), C5b–Sn1b–O1b 104.2(1), C5b–Sn1b–O1 109.7(1), O1a–Sn1b–O1b 150.7(1), O1a–Sn1b–O1 68.6(1), O1b–Sn1b–O1 82.0(1), Sn1a–O1a–Sn1b 96.7(1), Sn1a–O1–Sn1a^{i} 106.8(1), Sn1a–O1–Sn1b 121.3(1), Sn1a–O1–Sn1b^{i} 131.8(1) °. Symmetry transformation $i = -x,-y, 1-z$. Hydrogen bond: O2a···O2 2.779(5) Å.

– 152 ppm featuring a span of – 965 ppm and a skew of 0.38. Site 2 is found at $\delta_{iso} = -202$ ppm, and it has a skew of 0.38 and a slightly larger span of – 1041 ppm. The chemical shifts imply the existence of two five-coordinate tin sites in a *cis*-C_2SnO_3 trigonal-bipyramidal configuration as they are similar to the – 177 ppm value recorded for dibutyltin oxide.[16]

In centrosymmetric bis[1,1,3,3-tetraorganylbis-(carboxylato)distannoxanes], the most common configuration consists of one carboxylato group that is linked to the $Sn_{endocyclic}$–O–$Sn_{exocyclic}$ unit through the O–C–O group (giving rise to a six-membered $Sn_{endoccylic}$–O–$Sn_{exocyclic}$–O–C–O ring) and the other carboxylato group that is coordinated to the $Sn'_{endocyclic}$–O–$Sn_{exocyclic}$ unit through only one esteryl oxygen end (giving rise to a four-membered $Sn'_{endoccylic}$–O–$Sn_{exocyclic}$–O ring). In this configuration, the endocyclic tin atom is unambiguously six-coordinate whereas the exocyclic tin atom is only five-coordinate; such a configuration is adopted by bis[1,3-bis(*N,N*-diethylthiocarbamoylthioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxane].[17] Changes in the R group of the carboxylato unit usually result only in minor variations in the overall structures,[1] but in the (thiophene)gloxylato[18] and picolinato-*N*-oxide[19] derivatives the exocyclic tin atoms are seven-coordinate. On the other hand, when the $Sn_{endocyclic}$–O–$Sn_{exocyclic}$ unit is linked to the carboxylato anion through only one esteryl oxygen atom instead of through the O–C–O group, both the endocyclic tin atom and the exocyclic tin atom will be only five-coordinate.

Crystal Structure

The crystal structure of bis[1,3-bis(3-oxapentamethylenecarbomoylthioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxane] as its bis-ethanol solvate (Fig. 2) is in agreement with the spectroscopic assignments for the unsolvated compound. The

centrosymmetric bis[bis(carboxylato)tetraorganyldistannoxane] has both tin atoms in a *cis*-C_2SnO_3 geometry. One carboxylato group bridges two tin atoms (through one oxygen atom) [$Sn_{endocyclic}$–O = 2.238(2), $Sn_{exocyclic}$–O = 2.487(2) Å] whereas the other is bonded to only one [$Sn_{exocyclic}$–O = 2.122(2) Å]; the carboxyl oxygen atom is weakly linked [Sn···O = 3.813(2) Å] to the endocyclic tin atom. The carbonyl end of the latter anion interacts somewhat more strongly with the endocyclic tin atom [Sn···O = 2.684(2) Å], distorting its geometry towards a skew-trapezoidal bipyramid. The double bond carbonyl oxygen atom of the former anion, rather than that of the latter, forms a hydrogen bond with the lattice ethanol [O···O = 2.779(5) Å]. The ready loss of the lattice ethanol from the crystal structure is explained plausibly by the fact that each solvent molecule forms only one hydrogen bond with the distannoxane. Such a hydrogen-bonding interaction precludes the O2a oxygen atom from bonding to the exocyclic Sn1b tin atom. The hydrogen bond is shorter than that [O···O = 2.819(9) Å] found in bis(dicyclohexylammonium) aquadimethyldi(oxalato)stannate ethanol solvate;[20] this compound does not lose the lattice ethanol as the crystal structure is stabilized by hydrogen bonds involving the ammonium counterion. In the distannoxane, the C_2Sn skeletons are somewhat widened [C-$Sn_{endocyclic}$-C = 131.3(2) °, C-$Sn_{exocyclic}$-C = 131.5 (1) °] relative to the idealized angle of 120 °C; the angles are smaller than those [C-$Sn_{endocyclic}$-C = 143.3(3) °, C-$Sn_{exocyclic}$-C = 139.6(3) °] found in bis[1,3-bis(*N*,*N*-diethylthiocarbamoylthioacetato)-1,1,3,3-tetrabutyl-1,3-distannoxane], whose endocyclic tin atom is located in a distorted octahedral site.[17] In solution, the compound dissociates to lower-coordinate entities; the solution NMR (^{1}H, ^{13}C and ^{119}Sn) spectra that were recorded at different temperatures and at different field strengths could not be interpreted in terms of unique organotin species.

Crystal data

$C_{64}H_{124}N_4O_{20}S_4Sn_4$,
$[(C_4H_9)_8(C_7H_{10}NO_4S)_4(C_2H_6O)_2O_2Sn_4]$:
FW = 1872.67, triclinic, *P*−1, *a* = 12.1877(6) Å, *b* = 13.0141(7) Å, *c* = 13.6729(5) Å, α = 92.140(4) °, β = 93.510(4) °, γ = 105.384(5) °, *V* = 2083.8(2) Å^3, *Z* = 1, $D_{X\text{-ray}}$ = 1.492 g cm^{-3}, *F*(000) = 960, μ = 1.349 mm^{-1}.

In vitro antitumor activity

The anhydrous compound when screened against selected human tumor cell lines is more active *in vitro* than *cis*-platin, etoposide and 5-fluorouracil and only marginally less active than doxorubicin. For the two MCF-7 and WiDr cell lines, the ID_{50} values (MCF-7 41 ng ml^{-1}; WiDr 125 ng ml^{-1}) compare favorably with those obtained for $\{[(C_4H_9)_2SnO_2CC_6H_2\text{-}2,3,4(\text{-}OCH_3)_3]_2O\}_2$ (MCF-7 38 ng ml^{-1}; WiDr 323 ng ml^{-1}) and $\{[(C_4H_9)_2SnO_2CC_6H_3\text{-}4\text{-}NH_2\text{-}2\text{-}OH]_2O\}_2$ (MCF-7 42 ng ml^{-1}; WiDr 330 ng ml^{-1}) distannoxanes.[2]

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have been deposted with the Cambridge Crystallographic Database Centre as supplementary publication CCDC 118711 Copies of the available material can be obtained, free of charge, on application to the Cambridge Crystallographic Database Centre, 12 Union Road, Cambridge CS2 1EK, UK (e-mail: deposit@chemcrys.cam.ac.uk). The list of F_o/F_c data are available from the first author (S.W.N.) up to one year after the publication has appeared.

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