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Bis(dicyclohexylammonium) (oxalato)(pyridine-2,6-dicarboxylato) dibutylstannate 3.5 hydrate, the first crystallographic example of a mixed-chelate diorganotin(IV) compound

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Abstract

Bis(dicyclohexylammonium) (oxalato)(pyridine-2,6-dicarboxylato)dibutylstannate 3.5 hydrate is assigned a seven-coordinate geometry at the tin atom from solid-state spectroscopic measurements (CP/MAS $\delta(^{119}\text{Sn}) = -486$ ppm; $^{119\text{m}}\text{Mössbauer } \Delta = 4.15$ mm s $^{-1}$), and the assignment has been confirmed by low-temperature X-ray diffraction analysis. The ammonium stannate crystallizes as two independent ion pairs. In both anions, the tin atom is chelated by the pyridine-2,6-dicarboxylato and oxalato dianions, whose donor ends comprise the pentagonal plane of the *trans*-C $_2$ SnNO $_4$ pentagonal bipyramidal coordination polyhedron. The dibutyltin skeleton is almost linear (C–Sn–C = 173.9(2), 174.6(2) $^\circ$); the linearity is preserved in solution ($|^1J(^{119}\text{Sn}-^{13}\text{C})| = 1167.8$ Hz in chloroform). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; Mixed-chelate diorganotin

1. Introduction

On the basis of solution ^{119}Sn -NMR measurements, the tin atom in the series of mixed-chelate (CH $_3$) $_2$ Sn(PAN)(Ch) complexes [PAN = 1-(2-pyridylazo)-2-naphthalolato monoanion; Ch = β -diketonato, dithiocarbamato, oxinato, tropolonato, carboxylato monoanion] has been assigned a seven-coordinate *trans*-pentagonal bipyramidal geometry [1]. Diorganotin R $_2$ Sn(Ch')(Ch'') compounds that possess two different chelating groups are inherently unstable with respect to the symmetrical R $_2$ Sn(Ch') $_2$ and R $_2$ Sn(Ch'') $_2$ compounds owing to differences in the binding ability of the chelating entity. Curiously, despite the stability, and consequently, the peculiarity of the PAN complexes, none has been structurally verified. Besides these PAN complexes, few mixed-chelate diorganotin compounds have been reported [2] in the literature, in

contrast to the numerous reports of symmetrical bis-chelated six-coordinate diorganotin compounds, a number of which have been structurally verified [3]. This paper reports an extension of the PAN-Ch concept to the synthesis and structural characterization of mixed-chelate diorganotin compounds by the use of a pair of terdentate-bidentate dianions to bind to tin to confer seven-fold coordination to the tin atom. Since the R $_2$ Sn(Ch')(Ch'') entity (Scheme 1) possesses negative charges, two bulky dicyclohexylammonium cations are used as counterions to balance these.

2. Experimental

Dibutyltin oxide and 2,6-pyridinedicarboxylic acid (1/1 molar ratio) were heated in a small volume of ethanol to form bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] [4], which separated from solution as a solid. To the suspension was added an equimolar quantity of bis(dicyclohexylammonium) oxalate (prepared by treating dicyclohexylamine and oxalic acid dihydrate in a 2/1 molar ratio in a small quantity of ethanol). The

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Table 1

Atomic coordinates and equivalent isotropic temperature factors for bis(dicyclohexylammonium) (oxalato) (pyridine - 2,6 - dicarboxylato)-dibutylstannate 3.5 hydrate

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Sn1a	0.01901(2)	0.30406(1)	0.74063(1)	0.0278(2)
O1a	0.0999(2)	0.3686(1)	0.7126(1)	0.034(1)
O2a	0.1931(2)	0.4306(1)	0.7479(2)	0.041(1)
O3a	0.1150(2)	0.3324(1)	0.8214(1)	0.028(1)
O4a	0.2214(2)	0.3881(1)	0.8544(1)	0.037(1)
O5a	0.0071(2)	0.2600(1)	0.8194(1)	0.035(1)
O6a	0.0689(3)	0.1945(2)	0.8540(2)	0.058(1)
O7a	0.0339(3)	0.3037(2)	0.6390(2)	0.046(1)
O8a	0.1078(3)	0.2617(2)	0.5608(2)	0.061(1)
O9a	0.1301(3)	0.3502(2)	0.5914(2)	0.069(1)
O10a	0.0005(4)	0.3084(2)	0.4992(2)	0.088(2)
O11a	-0.1312(4)	0.3674(2)	0.4280(2)	0.088(2)
N1a	-0.0887(2)	0.2420(2)	0.7118(2)	0.032(1)
N2a	0.1829(3)	0.4976(2)	0.6555(2)	0.037(1)
N3a (50%)	0.097(1)	0.2569(8)	0.936(2)	0.033(2)
N3' (50%)	0.105(1)	0.2518(9)	0.940(2)	0.033(2)
C1a	0.1206(3)	0.2551(2)	0.7253(2)	0.036(1)
C2a	0.1000(3)	0.2001(2)	0.7143(2)	0.035(1)
C3a	0.1788(4)	0.1709(2)	0.7022(3)	0.045(1)
C4a	0.1618(4)	0.1150(2)	0.6968(3)	0.051(2)
C5a	-0.0813(3)	0.3569(2)	0.7476(2)	0.036(1)
C6a	-0.0578(4)	0.3999(2)	0.7894(3)	0.046(1)
C7a	-0.1355(4)	0.4347(2)	0.7911(3)	0.051(2)
C8a	-0.1114(6)	0.4773(3)	0.8340(4)	0.103(3)
C9a	0.1514(3)	0.3920(2)	0.7532(2)	0.029(1)
C10a	0.1638(3)	0.3689(2)	0.8156(2)	0.027(1)
C11a	-0.0590(3)	0.2221(2)	0.8137(2)	0.037(1)
C12a	-0.1074(3)	0.2114(2)	0.7522(2)	0.036(1)
C13a	-0.1644(3)	0.1712(2)	0.7362(3)	0.045(1)
C14a	-0.2003(4)	0.1636(2)	0.6778(3)	0.053(2)
C15a	-0.1791(4)	0.1952(2)	0.6366(3)	0.051(2)
C16a	-0.1210(3)	0.2346(2)	0.6547(2)	0.038(1)
C17a	-0.0861(4)	0.2696(2)	0.6143(2)	0.046(1)
C18a	0.2221(4)	0.4673(2)	0.6128(2)	0.041(1)
C19a	0.2171(4)	0.4944(2)	0.5549(2)	0.050(2)
C20a	0.2604(5)	0.4625(3)	0.5146(3)	0.062(2)
C21a	0.3557(4)	0.4490(2)	0.5423(3)	0.057(2)
C22a	0.3611(5)	0.4239(2)	0.6011(3)	0.057(2)
C23a	0.3178(4)	0.4557(2)	0.6415(2)	0.046(1)
C24a	0.0888(4)	0.5151(2)	0.6369(2)	0.044(1)
C25a	0.0249(4)	0.4724(3)	0.6192(3)	0.072(2)
C26a	-0.0707(5)	0.4930(4)	0.6034(4)	0.101(3)
C27a	-0.0943(5)	0.5240(4)	0.6535(4)	0.097(3)
C28a	-0.0278(5)	0.5653(4)	0.6702(4)	0.083(2)
C29a	0.0671(4)	0.5449(3)	0.6875(3)	0.062(2)
C30a (50%)	0.1151(6)	0.3097(4)	0.9583(4)	0.035(2)
C31a (50%)	0.0229(6)	0.3334(3)	0.9472(5)	0.040(2)
C32a (50%)	0.0341(8)	0.3886(4)	0.9656(5)	0.048(2)
C33a (50%)	0.077(3)	0.394(2)	1.0310(7)	0.050(4)
C34a (50%)	0.167(4)	0.3678(8)	1.040(2)	0.049(5)
C35a (50%)	0.1592(8)	0.3122(4)	1.0233(4)	0.043(2)
C36a (50%)	0.1768(9)	0.2230(5)	0.9399(6)	0.028(3)
C37a (50%)	0.2583(6)	0.2480(4)	0.9281(5)	0.043(2)
C38a (50%)	0.3346(7)	0.2097(4)	0.9382(5)	0.053(2)
C39a (50%)	0.3120(1)	0.1610(5)	0.9037(7)	0.049(3)
C40a (50%)	0.2284(7)	0.1389(4)	0.9166(5)	0.051(2)
C41a (50%)	0.1517(8)	0.1763(4)	0.9023(6)	0.055(3)
C30' (50%)	0.1072(6)	0.2913(3)	0.9861(5)	0.035(2)
C31' (50%)	0.0139(6)	0.3134(4)	0.9815(4)	0.040(2)
C32' (50%)	0.0157(8)	0.3518(4)	1.0305(5)	0.048(2)
C33' (50%)	0.085(3)	0.392(2)	1.0254(9)	0.050(4)
C34' (50%)	0.178(4)	0.3704(9)	1.030(2)	0.049(5)
C35' (50%)	0.1745(7)	0.3317(4)	0.9812(5)	0.043(2)

Table 1 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
C36' (50%)	0.1931(1)	0.2338(5)	0.9273(5)	0.028(3)
C37' (50%)	0.2382(7)	0.2058(4)	0.9829(4)	0.043(2)
C38' (50%)	0.3241(7)	0.1825(5)	0.9722(5)	0.053(2)
C39' (50%)	0.302(1)	0.1455(5)	0.9207(5)	0.049(3)
C40' (50%)	0.2537(8)	0.1725(4)	0.8653(5)	0.051(2)
C41' (50%)	0.1693(7)	0.1981(5)	0.8748(6)	0.055(3)
Sn1b	0.51958(2)	0.17439(1)	0.74968(1)	0.0284(1)
O1b	0.5969(2)	0.1116(1)	0.7135(1)	0.033(1)
O2b	0.7022(2)	0.0538(1)	0.7406(2)	0.040(1)
O3b	0.6209(2)	0.1430(1)	0.8250(1)	0.035(1)
O4b	0.7279(2)	0.0869(1)	0.8525(2)	0.041(1)
O5b	0.5063(2)	0.2185(1)	0.8326(2)	0.040(1)
O6b	0.4496(3)	0.2816(2)	0.8732(2)	0.077(2)
O7b	0.4518(2)	0.1756(1)	0.6507(2)	0.038(1)
O8b	0.3713(3)	0.2192(2)	0.5762(2)	0.060(1)
O9b	0.3679(3)	0.3505(2)	0.9312(2)	0.072(2)
O10b	0.4335(3)	0.3886(1)	1.0398(2)	0.051(1)
O11b	0.6097(2)	0.3671(1)	1.0900(2)	0.043(1)
O12b	0.5469(3)	0.2680(2)	1.0504(2)	0.056(1)
N1b	0.4125(2)	0.2378(2)	0.7284(2)	0.029(1)
N2b	0.6934(3)	-0.0155(1)	0.6498(2)	0.029(1)
N3b	0.6171(3)	0.2300(2)	0.9557(2)	0.033(1)
C1b	0.6181(3)	0.2232(2)	0.7293(2)	0.033(1)
C2b	0.5983(3)	0.2784(2)	0.7200(2)	0.036(1)
C3b	0.6752(3)	0.3075(2)	0.7049(3)	0.042(1)
C4b	0.6552(4)	0.3625(2)	0.6960(3)	0.059(2)
C5b	0.4203(4)	0.1231(2)	0.7619(3)	0.047(1)
C6b	0.4472(4)	0.0758(2)	0.7958(3)	0.049(1)
C7b	0.3685(4)	0.0431(2)	0.8012(3)	0.054(2)
C8b	0.3948(7)	-0.0025(3)	0.8374(4)	0.111(4)
C9b	0.6554(3)	0.0884(2)	0.7507(2)	0.030(1)
C10b	0.6697(3)	0.1072(2)	0.8155(2)	0.030(1)
C11b	0.4552(4)	0.2556(2)	0.8307(2)	0.044(1)
C12b	0.4008(3)	0.2686(2)	0.7709(2)	0.033(1)
C13b	0.3471(3)	0.3103(2)	0.7591(2)	0.038(1)
C14b	0.3067(3)	0.3198(2)	0.7014(2)	0.039(1)
C15b	0.3204(3)	0.2879(2)	0.6577(2)	0.035(1)
C16b	0.3745(3)	0.2469(2)	0.6727(2)	0.029(1)
C17b	0.4000(3)	0.2107(2)	0.6291(2)	0.037(1)
C18b	0.5999(3)	-0.0342(2)	0.6312(2)	0.034(1)
C19b	0.5743(4)	-0.0571(2)	0.6851(2)	0.041(1)
C20b	0.4795(4)	-0.0774(3)	0.6698(3)	0.057(2)
C21b	0.4147(4)	-0.0370(3)	0.6440(3)	0.062(2)
C22b	0.4410(4)	-0.0130(3)	0.5910(3)	0.057(2)
C23b	0.5356(3)	0.0072(2)	0.6060(2)	0.042(1)
C24b	0.7345(3)	0.0114(2)	0.6051(2)	0.031(1)
C25b	0.8286(3)	0.0260(2)	0.6347(2)	0.036(1)
C26b	0.8727(4)	0.0548(2)	0.5922(3)	0.048(1)
C27b	0.8725(4)	0.0241(2)	0.5369(3)	0.048(1)
C28b	0.7785(4)	0.0081(2)	0.5084(2)	0.043(1)
C29b	0.7340(4)	-0.0206(2)	0.5509(2)	0.036(1)
C30b	0.6381(3)	0.1756(2)	0.9677(2)	0.033(1)
C31b	0.5514(4)	0.1466(2)	0.9579(3)	0.043(1)
C32b	0.5704(4)	0.0912(2)	0.9690(3)	0.050(2)
C33b	0.6245(5)	0.0826(2)	1.0305(3)	0.063(2)
C34b	0.7094(5)	0.1126(2)	1.0406(3)	0.060(2)
C35b	0.6923(4)	0.1683(2)	1.0291(2)	0.044(1)
C36b	0.6939(3)	0.2627(2)	0.9492(2)	0.035(1)
C37b	0.7179(4)	0.2540(2)	0.8904(3)	0.044(1)
C38b	0.7940(4)	0.2877(2)	0.8824(3)	0.055(2)
C39b	0.7735(5)	0.3418(2)	0.8921(3)	0.059(2)
C40b	0.7479(6)	0.3498(2)	0.9492(3)	0.074(2)
C41b	0.6705(5)	0.3163(2)	0.9566(3)	0.058(2)

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

mixture was briefly heated to dissolve the reactants. The evaporation of the solvent gave a tan colored semi-solid, and the addition of ether yielded bis(dicyclohexylammonium) (oxalato)(pyridine-2,6-dicarboxylato)-dibutylstannate 3.5 hydrate as a white powder. The compound was purified by using ether to precipitate the compound out of its solution in chloroform. Colorless single crystals were obtained by the use of ethanol as the solvent for recrystallization. Carbon-13-NMR chemical shift δ (coupling constants in parenthesis) for [(cyclo-C₆H₁₁)₂NH₂]₂[(C₄H₉)₂Sn(C₂O₄)(C₇H₃NO₄)]·3.5H₂O in CDCl₃: butyl $C_\alpha = 32.9$ (1167.8 Hz), $C_\beta = 27.9$ (44.6 Hz), $C_\gamma = 26.5$ (174.4 Hz), $C_\delta = 13.4$ (14.5 Hz); cyclohexyl $C_1 = 53.6$, $C_2 = 29.5$, $C_3 = 24.6$, $C_4 = 25.0$; pyridyl $C_o = 141.3$, $C_m = 126.0$, $C_p = 147.2$; carboxyl -CO₂ = 166.3, 166.4 ppm. Tin-119m Mössbauer (78 K): Isomer shift = 1.30 mm s⁻¹, $\Delta = 4.15$ mm s⁻¹; $\Gamma_1 = 1.00$ mm s⁻¹, $\Gamma_2 = 1.16$ mm s⁻¹. Solid-state ¹¹⁹Sn-NMR (relative to tetramethyltin): $\delta = -486$ ppm.

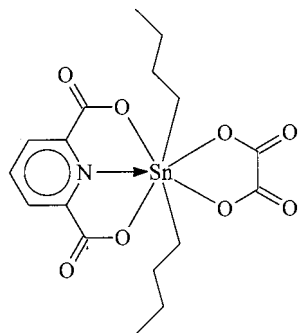
A 0.85 × 0.55 × 0.40 mm³ crystal was used for the low-temperature (-115°C) diffraction measurements on a Siemens CCD area-detector diffractometer (Mo-K α , $\lambda = 0.71073$ Å) [5]. The absorption-corrected [6] set of intensities at $2\theta = 50^\circ$ consisted of 109 487 reflections ($-18 \leq h \leq 18$, $-20 \leq k \leq 31$, $27 \leq l \leq 27$) that were averaged to furnish 16 719 independent reflections ($R_{\text{int}} = 0.043$). The structure was solved by direct methods [7] and refined on F^2 [8]. One of the dicyclohexylammonium cations is disordered, and this cation was refined as two cations of half-site occupancy; the carbon-carbon distances were DFIXED at C-C = 1.54 ± 0.01 Å and the unprimed and primed atoms were restrained to have identical temperature factors. Additionally, the four nitrogen-carbon distances are restrained with a SADI instruction. During the later stages of refinement, the difference Fourier had a peak of 2.02 e Å⁻³ at 0.0316, 0.4200, 0.4910; peaks larger than 1 e Å⁻³ were also found near the Sn atoms. PLATON [9] suggested that this site was too small (13.8 Å³) for a water molecule although it was within hydrogen bonding interaction with other oxy-

gen atoms. Refinement of this site as an oxygen atom led to large temperature factors. The SQUEEZE option in PLATON was applied to the reflection data. This resulted in smearing the excess electron density, so that the large peaks in the final difference Fourier were only found near the Sn atoms. The final difference Fourier had peaks ranging from -1.166 to 1.679 e Å⁻³. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were generated and allowed to ride on their parent C- or N-atoms with $U = 1.5U_{\text{eq}}(\text{C,N})$; the water H-atoms were placed at calculated positions and refined with U fixed at 0.10 Å². The refinements converged to a final R index of 0.072 for all reflections and 0.061 for 13759 $I \geq 2\sigma(I)$ reflections. Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1. The structure of the dianion is shown in as an ORTEP [10] plot at the 50% probability level in Fig. 1. Fig. 2 shows the packing.

Crystal data: C₄₁H₆₉N₃O₈Sn·3.5H₂O, $M_r = 913.74$, monoclinic, $P2_1/c$, $a = 15.444(4)$ Å, $b = 26.853(7)$ Å, $c = 23.420(7)$ Å, $\beta = 102.03(4)^\circ$, $V = 9499(5)$ Å³, $\rho_{\text{calc}} = 1.278$ g cm⁻³, $F(000) = 3880$, $\mu = 0.595$ mm⁻¹ for $Z = 8$.

3. Results and discussion

From the magnitude of the Mössbauer quadrupole splitting ($QS = 4.15$ mm s⁻¹) for mixed-chelate bis(dicyclohexylammonium) (oxalato)(pyridine-2,6-dicarboxylato)dibutylstannate, the point-charge model [11] predicts a linear dibutyltin skeleton having the tin atom either in a six-coordinate *trans*-octahedral or a seven-coordinate *trans*-pentagonal bipyramidal environment [12]. The quadrupole splitting is similar to that ($\Delta = 4.06$ mm s⁻¹) found in bis(dicyclohexylammonium) bis(pyridine-2,6-dicarboxylato)dibutylstannate (C-Sn-C = 168.9(5)°) [13] as well as that ($\Delta = 4.18$ mm s⁻¹) found in bis(dicyclohexylammonium) μ -oxalato-bis(aqua-oxalato)dibutylstannate (C-Sn-C = 172.2(3)°) [14]; the tin atoms in both stannates display *trans*-pentagonal bipyramidal coordination. For the mixed-chelated stannate, a seven-coordinate assignment that implicates a chelating pyridine-2,6-dicarboxylato group is more plausible than a six-coordinate assignment since this dianion, as well as the *p*-hydroxy substituted analog (the 4-hydroxypyridine-2,6-dicarboxylato dianion), are known to chelate to tin in other dibutyltin and dibutylstannate systems [15]. The seven-coordinate assignment for the mixed-chelate stannate is also supported by the solid-state tin-119 chemical shift ($\delta = -486$ ppm), which falls within the range recorded for the PAN complexes [1,12] mentioned earlier.



Scheme 1.

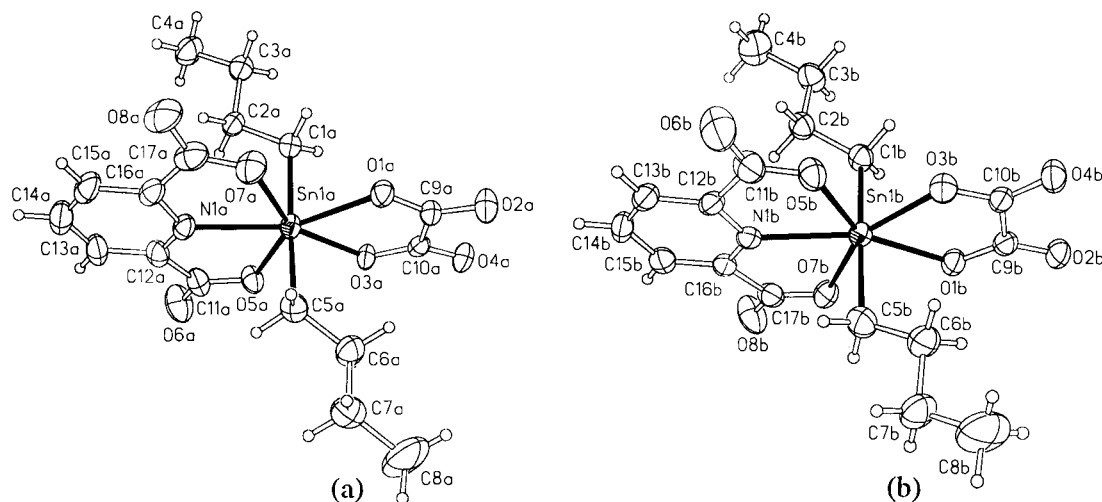


Fig. 1. (a) ORTEP plot of the (oxalato)(pyridine-2,6-dicarboxylato)dibutylstannate dianion of the *a* ion-pair of bis(dicyclohexylammonium)-(oxalato)(pyridine-2,6-dicarboxylato)dibutylstannate 3.5 hydrate at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles: Sn1a–C1a = 2.134(5) Å, Sn1a–C5a = 2.132(5) Å, Sn1a–N1a = 2.353(4) Å, Sn1a–O1a = 2.310(3) Å, Sn1a–O3a = 2.277(3) Å, Sn1a–O5a = 2.297(3) Å, Sn1a–O7a = 2.349(4) Å; C1a–Sn1a–C5a = 173.9(2)°, C1a–Sn1a–N1a = 90.9(2)°, C1a–Sn1a–O1a = 87.4(2)°, C1a–Sn1a–O3a = 88.4(2)°, C1a–Sn1a–O5a = 94.4(2)°, C1a–Sn1a–O7a = 86.5(2)°, C5a–Sn1a–N1a = 90.7(2)°, C5a–Sn1a–O1a = 88.1(2)°, C5a–Sn1a–O3a = 94.0(2)°, C5a–Sn1a–O5a = 91.7(2)°, C5a–Sn1a–O7a = 88.7(2)°, N1a–Sn1a–O1a = 147.3(1)°, N1a–Sn1a–O3a = 140.7(1)°, N1a–Sn1a–O5a = 68.5(1)°, N1a–Sn1a–O7a = 68.3(1)°, O1a–Sn1a–O3a = 71.9(1)°, O1a–Sn1a–O5a = 144.2(1)°, O1a–Sn1a–O7a = 79.0(1)°, O3a–Sn1a–O5a = 72.4(1)°, O3a–Sn1a–O7a = 150.6(1)°, O5a–Sn1a–O7a = 136.8(1)°. (b) ORTEP plot of the (oxalato)(pyridine-2,6-dicarboxylato)dibutylstannate dianion of the *b* ion-pair of bis(dicyclohexylammonium)-(oxalato)(pyridine-2,6-dicarboxylato)dibutylstannate 3.5 hydrate at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles: Sn1b–C1b = 2.136(5) Å, Sn1b–C5b = 2.125(6) Å, Sn1b–N1b = 2.353(4) Å, Sn1b–O1b = 2.326(3) Å, Sn1b–O3b = 2.263(3) Å, Sn1b–O5b = 2.320(3) Å, Sn1b–O7b = 2.336(4) Å; C1b–Sn1b–C5b = 174.6(2)°, C1b–Sn1b–N1b = 90.6(2)°, C1b–Sn1b–O1b = 85.4(2)°, C1b–Sn1b–O3b = 89.7(2)°, C1b–Sn1b–O5b = 93.7(2)°, C1b–Sn1b–O7b = 87.9(2)°, C5b–Sn1b–N1b = 90.2(2)°, C5b–Sn1b–O1b = 91.1(2)°, C5b–Sn1b–O3b = 93.1(2)°, C5b–Sn1b–O5b = 91.5(2)°, C5b–Sn1b–O7b = 87.5(2)°, N1b–Sn1b–O1b = 147.0(1)°, N1b–Sn1b–O3b = 140.9(1)°, N1b–Sn1b–O5b = 68.1(1)°, N1b–Sn1b–O7b = 68.3(1)°, O1b–Sn1b–O3b = 71.9(1)°, O1b–Sn1b–O5b = 144.8(1)°, O1b–Sn1b–O7b = 78.8(1)°, O3b–Sn1b–O5b = 72.9(1)°, O3b–Sn1b–O7b = 150.7(1)°, O5b–Sn1b–O7b = 136.4(1)°.

The bis(pyridine-2,6-dicarboxylato)dibutylstannate and bis(oxalato)dibutylstannate as their bis(dicyclohexylammonium) salts represent two examples of symmetrical bischelated diorganostannates, i.e. diorganotin compounds whose tin atoms are covalently bonded to two dianions. Chelation by the two oxalato dianions in bis(dicyclohexylammonium) bis(oxalato)dibutylstannate results in 6-fold coordination for the tin atom [14]; on the other hand, in bis(dicyclohexylammonium) bis(pyridine-2,6-dicarboxylato)dibutylstannate, which has been crystallographically examined as a monohydrate, one of the pyridine-2,6-dicarboxylato dianions chelates in an *O,N,O* manner whereas the other binds through both oxygen ends of only one carboxyl–CO₂ fragment [13]. The two oxalato entities display bites (i.e. O–Sn–O angle) of 72.8(1)° whereas the pyridine-2,6-dicarboxylato entity shows a bite (i.e. O–Sn–O angle) of 139.7(2)°. The bite angles (oxalato bite = 71.9(1) and 71.9(1)°; pyridine-2,6-dicarboxylato bite = 136.4(1) and 136.8(1)°) found in bis(dicyclohexylammonium) (pyridine-2,6-dicarboxylato)(oxalato)dibutylstannate, which shows seven-coordinate tin, compare well with the reported bite angles.

The (pyridine-2,6-dicarboxylato)(oxalato)dibutylstan-

nate dianion (Fig. 1) has its tin atom in a *trans*-pentagonal bipyramidal polyhedron, whose pentagonal plane is made up of the donor ends of the oxalato and pyridine-2,6-dicarboxylato dianions. In the pentagonal plane, the five adjacent angles subtended at tin (angles in anion *a* = 71.9(1), 72.4(1), 68.5(1), 68.3(1) and 79.0(1)°; angles in anion *b* = 71.9(1), 72.9(1), 68.1(1), 68.3(1) and 78.8(1)°) add up to exactly 360°; there is a relatively small spread in the angles, unlike the large spread noted in other seven-coordinate dibutyltin and dibutylstannate structures [13–15]. Hydrogen bonds link the dicyclohexylammonium cations, stannate anions and lattice water molecules into a infinite layer structure (Fig. 2). These species do not pack compactly in the crystal structure, and there are voids in the unit cell, although none of the voids is large enough to accommodate a water molecule. A similar less-than-compact arrangement is also noted in the bis(dicyclohexylammonium) (oxalato)(4-hydroxypyridine-2,6-dicarboxylato)dibutylstannate, which crystallizes with half a molecule each of water and ethanol [C₄₁H₆₉N₃O₉Sn_{0.5}H₂O·0.5C₂H₆O, monoclinic, *P*2₁/*n*, *a* = 20.495(1) Å, *b* = 22.773(1) Å, *c* = 21.635(1) Å, β = 104.79(1)°, *V* = 9763(1) Å³]. This compound also be-

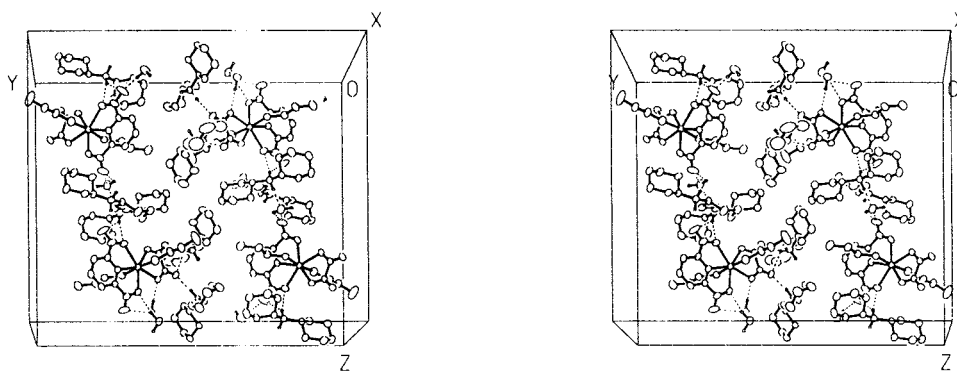


Fig. 2. ORTEP stereoplot of the packing of bis(dicyclohexylammonium)(oxalato)(pyridine-2,6-dicarboxylato)dibutylstannate 3.5 hydrate at the 50% probability level. Hydrogen atoms belonging to the ammonium cations and water molecules are not drawn. The disorder in one of the dicyclohexylammonium cations is not shown. Hydrogen bonds: $N2a \cdots O2a = 2.793(6)$ Å, $N2a \cdots O2b^i = 3.089(6)$ Å, $N2a \cdots O4b^i = 2.791(6)$ Å, $N3a \cdots O5a = 2.87(4)$ Å, $N3a \cdots O10a^{ii} = 2.90(3)$ Å, $N3' \cdots O5a = 3.00(4)$ Å, $N3' \cdots O10a^{ii} = 2.84(3)$ Å, $O9a \cdots O1a = 3.012(5)$ Å, $O9a \cdots O10a = 2.850(7)$ Å, $O10a \cdots O8a = 2.731(8)$ Å, $O10a \cdots O9a = 2.850(7)$ Å, $O10a \cdots O11a = 2.830(8)$ Å, $O11a \cdots O4b^{iii} = 2.786(7)$ Å, $O11a \cdots O6a^{iv} = 2.718(7)$ Å, $N2b \cdots O2a^v = 3.026(6)$ Å, $N2b \cdots O4a^v = 2.915(4)$ Å, $N2b \cdots O2b = 2.808(6)$ Å, $N3b \cdots O5b = 3.045(6)$ Å, $N3b \cdots O12b = 2.853(7)$ Å, $O9b \cdots O4a = 2.770(6)$ Å, $O9b \cdots O6b = 2.752(7)$ Å, $O9b \cdots O10b = 2.732(6)$ Å, $O10b \cdots O7b^{ii} = 3.081(6)$ Å, $O10b \cdots O11b = 2.790(6)$ Å, $O11b \cdots O1b = 2.995(5)$ Å, $O11b \cdots O12b = 2.917(6)$ Å, $O12b \cdots O8b^{ii} = 2.919(7)$ Å. Symmetry transformation: $i = 1 - x, -y, 1 - z$; $ii = x, 1/2 - y, 1/2 + z$; $iii = x - 1, 1/2 - y, z - 1/2$; $iv = 1 - x, -1 - y, 1 - z$; $v = x, 1/2 - y, 1/2 + z$.

longs to a centrosymmetric space group, and there are also two formula units per asymmetric unit. The structure is disordered at room temperature (as well as at -115°C), and the disorder required a large number of restraints for the refinements to converge. Nevertheless, the stereochemical features of the two stannate dianions in the compound have been reliably determined; one of the two dianions is shown in Fig. 3. The 4-hydroxy group is engaged in hydrogen bonding interactions, but the acceptor atoms are different for the two ion-pairs. Nevertheless, bond dimensions involving the tin atom

are similar in both compounds; the two compounds differ mainly in the hydrogen bonding interactions.

The magnitude of the one-bond coupling constant ($|J^1(^{119}\text{Sn}-^{13}\text{C})| = 1167.8$ Hz) of bis(dicyclohexylammonium)(oxalato)(pyridine-2,6-dicarboxylato)dibutylstannate 3.5 hydrate in solution, which has been correlated with the carbon–tin–carbon angle derived from diffraction measurements [16], implies that the linearity of the dibutyltin skeleton (and, by extension, the seven-coordinate geometry) is preserved in chloroform.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 116028. Copies of the available material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk). The list of F_o/F_c data is available from the author (e-mail: inswen@umcsd.um.edu.my) up to one year after the publication has appeared.

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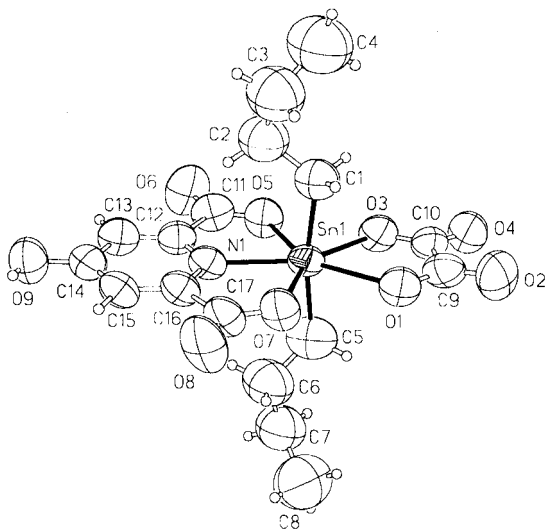


Fig. 3. ORTEP plot of the one of the two (oxalato)(4-hydroxypyridine-2,6-dicarboxylato)dibutylstannate dianions of bis(dicyclohexylammonium)(oxalato)(4-hydroxypyridine-2,6-dicarboxylato)dibutylstannate hemihydrate hemimethanol solvate at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii.

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