

Reactions of tin tetrachloride with diethyl glutarate. Crystal structures of $[\text{Sn}_2\text{Cl}_8\{\mu\text{-C}_3\text{H}_6(\text{CO}_2\text{Et})_2\}_2]\cdot 2\text{CH}_2\text{Cl}_2$ and *cis*- $[\text{SnCl}_4(\text{H}_2\text{O})_2]\cdot \text{C}_3\text{H}_6(\text{CO}_2\text{Et})_2$.

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The dimeric compound $[\text{Sn}_2\text{Cl}_8\{\mu\text{-C}_3\text{H}_6(\text{CO}_2\text{Et})_2\}_2]\cdot 2\text{CH}_2\text{Cl}_2$ **1** has been prepared by direct reaction of SnCl_4 with diethyl glutarate in CH_2Cl_2 and its crystal structure has been determined. Each tin atom is octahedrally co-ordinated by four chlorine atoms and two mutually *cis* carbonyl oxygen atoms of two bridging diethyl glutarate molecules. During the crystallization of **1** the compound *cis*- $[\text{SnCl}_4(\text{H}_2\text{O})_2]\cdot \text{C}_3\text{H}_6(\text{CO}_2\text{Et})_2$ **2** was formed under the influence of moisture. Its crystal structure revealed a monomeric complex of Sn^{IV} in which each tin atom is surrounded octahedrally by four chlorine atoms and two water oxygen atoms. A non-co-ordinated ester molecule is hydrogen bonded through carbonyl oxygen atoms to one water molecule.

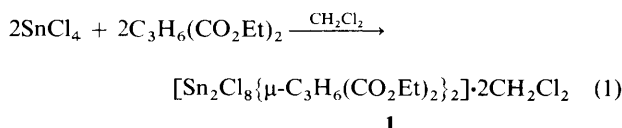
It is well established that titanium(IV) chloride and aromatic *o*-phthalate diesters form monomeric $[\text{TiCl}_4\{o\text{-C}_6\text{H}_4(\text{CO}_2\text{R})_2\}]$ complexes ($\text{R} = \text{Et}$,¹ Bu ,² or $\text{CH}_2\text{CH}_2\text{Ph}$ ³) while *m*-phthalate diesters form dimeric compounds of the formula $[\text{Ti}_2\text{Cl}_8\{\mu\text{-}m\text{-C}_6\text{H}_4(\text{CO}_2\text{R})_2\}_2]$ ($\text{R} = \text{Et}$ ⁴ or $\text{CH}_2\text{CH}_2\text{Ph}$ ⁵). In contrast, *para* diesters form linear polymers in which the dimeric units $\text{Cl}_3\text{Ti}(\mu\text{-Cl})_2\text{TiCl}_3$ are linked by diester molecules to the metal sites by carbonyl oxygen atoms.² A deeper understanding of conformational preferences of co-ordinated diester molecules with different metal atoms is of great importance because organic esters improve the stereospecificity of the high-activity Ziegler–Natta catalyst system based on AlEt_3 and titanium halides supported on activated MgCl_2 .⁶

We describe here a new simple high-yield method of synthesis leading to the dimeric compound $[\text{Sn}_2\text{Cl}_8\{\mu\text{-C}_3\text{H}_6(\text{CO}_2\text{Et})_2\}_2]\cdot 2\text{CH}_2\text{Cl}_2$. We isolated also, in the first place by accident, a species analysing for $\text{SnCl}_4\cdot 2\text{H}_2\text{O}$ from the solution during recrystallization of the dimer in dichloromethane. It had previously been shown that from a freshly opened commercial sample of $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$, *cis*- $[\text{SnCl}_4(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$ and a small amount of the dimeric compound $[\text{Sn}_2(\mu\text{-OH})_2\text{Cl}_6(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ could be obtained.⁷ The crystal structures of $[\text{Sn}_2\text{Cl}_8\{\mu\text{-C}_3\text{H}_6(\text{CO}_2\text{Et})_2\}_2]\cdot 2\text{CH}_2\text{Cl}_2$ and *cis*- $[\text{SnCl}_4(\text{H}_2\text{O})_2]\cdot \text{C}_3\text{H}_6(\text{CO}_2\text{Et})_2$ have now been determined.

Results and Discussion

Synthesis and structure of $[\text{Sn}_2\text{Cl}_8\{\mu\text{-C}_3\text{H}_6(\text{CO}_2\text{Et})_2\}_2]\cdot 2\text{CH}_2\text{Cl}_2$

The direct reaction of SnCl_4 with diethyl glutarate in 1 : 1 molar ratio in CH_2Cl_2 at room temperature yields an air-sensitive, colourless compound of composition $\text{SnCl}_4\cdot \text{C}_3\text{H}_6(\text{CO}_2\text{Et})_2\cdot \text{CH}_2\text{Cl}_2$, which can be stored under N_2 [equation (1)]. The IR



spectrum shows stretching $\nu(\text{C}=\text{O})$ modes at 1628s and 1620s cm^{-1} characteristic for co-ordinated ester molecules and bands at 354m and 328m cm^{-1} due to $\nu(\text{Sn}-\text{Cl})$ and $\nu(\text{Sn}-\text{O})$ vibrations. Compound **1** is well soluble in halogenated hydrocarbons, but it is insoluble in aromatic and aliphatic hydrocarbons.

Complex **1** is dimeric in the crystalline state. Its structure is depicted in Fig. 1. Interatomic distances, bond angles and

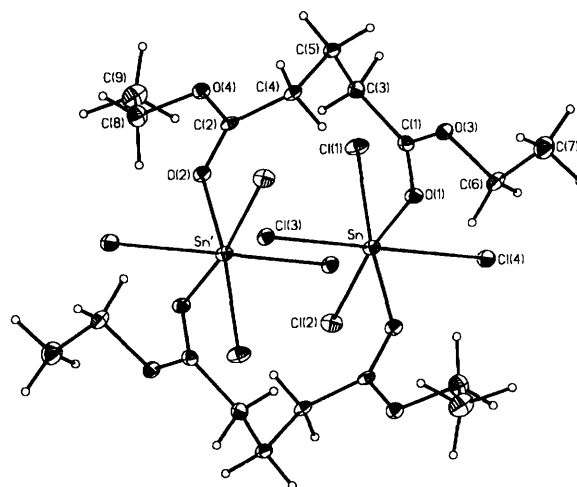


Fig. 1 Structure and numbering scheme of $[\text{Sn}_2\text{Cl}_8\{\mu\text{-C}_3\text{H}_6(\text{CO}_2\text{Et})_2\}_2]$ (solvate CH_2Cl_2 molecules are omitted for clarity)

selected torsion angles are listed in Table 1. In the centrosymmetric molecule four Cl atoms and two O atoms from two diethyl glutarate ligands (in *cis* position) form a distorted octahedron around the tin atom. Each of the diethyl glutarates is co-ordinated to two tin atoms *via* two carbonyl oxygen atoms. The non-hydrogen atoms of the two bridging ligands and the two tin atoms form a sixteen-membered ring. The $\text{Sn}-\text{O}(1)$ bond length of 2.190(3) and $\text{Sn}'-\text{O}(2)$ distance of 2.166(3) Å are slightly shorter than the average $\text{Sn}-\text{O}$ (carbonyl) bond length obtained from a search of the Cambridge Structural Database [$\text{Sn}-\text{O}$ 2.3(1)].⁸ The $\text{Sn}-\text{Cl}$ bond lengths (see Table 1) are similar to those found in *trans*- $[\text{SnCl}_4(\text{PhCH}=\text{CHCO}_2\text{Et})_2]$.⁹ The $\text{O}(1)-\text{C}(1)$ and $\text{O}(2)-\text{C}(2)$ carbonyl groups are in the preferred synperiplanar conformation to the $\text{O}(3)-\text{C}(6)$ and $\text{O}(4)-\text{C}(8)$ bonds, respectively. The two planar CO_2 groups of the diester molecule form an angle of 63.9°. The torsion angles $\text{Sn}-\text{O}(1)-\text{C}(1)-\text{C}(3)$ and $\text{Sn}'-\text{O}(2)-\text{C}(2)-\text{C}(4)$ of $-2.7(6)$ and $-11.4(6)^\circ$, respectively, show the tin atom to be co-ordinated in the plane formed by atoms $\text{O}(1)$, $\text{C}(1)$, $\text{O}(3)$ and $\text{C}(3)$ but out of the plane formed by $\text{O}(2)$, $\text{C}(2)$, $\text{O}(4)$ and $\text{C}(4)$. No inter- and intra-molecular contacts are observed in the crystal.

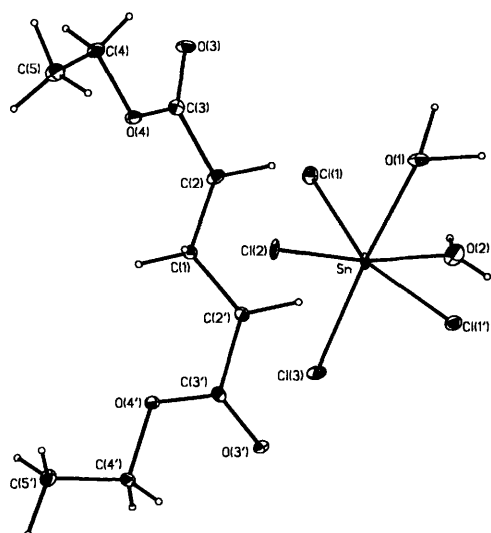
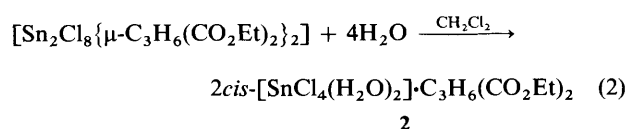
Synthesis and structure of *cis*- $[\text{SnCl}_4(\text{H}_2\text{O})_2]\cdot \text{C}_3\text{H}_6(\text{CO}_2\text{Et})_2$

During slow crystallization of **1** from CH_2Cl_2 a new crystalline complex, containing H_2O was formed [equation (2)], which is

Table 1 Interatomic bond distances (Å), angles (°) and torsion angles with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Sn–Cl(1)	2.375(1)	O(3)–C(6)	1.466(5)
Sn–Cl(2)	2.369(1)	O(4)–C(2)	1.312(5)
Sn–Cl(3)	2.382(1)	O(4)–C(8)	1.466(6)
Sn–Cl(4)	2.359(1)	C(1)–C(3)	1.479(6)
Sn–O(1)	2.190(3)	C(2)–C(4)	1.488(6)
Sn'–O(2)	2.166(3)	C(3)–C(5)	1.536(6)
O(1)–C(1)	1.247(5)	C(4)–C(5)	1.528(6)
O(2)–C(2)	1.240(5)	C(6)–C(7)	1.503(7)
O(3)–C(1)	1.305(5)	C(8)–C(9)	1.489(8)
Cl(1)–Sn–Cl(2)	98.9(1)	Sn–O(1)–C(1)	139.9(3)
Cl(1)–Sn–Cl(3)	93.1(1)	Sn'–O(2)–C(2)	139.1(3)
Cl(1)–Sn–Cl(4)	93.8(1)	O(1)–C(1)–O(3)	119.4(4)
Cl(1)–Sn–O(1)	92.9(1)	O(1)–C(1)–C(3)	125.8(4)
Cl(1)–Sn–O(2)	169.4(1)	O(2)–C(2)–O(4)	120.1(4)
Cl(2)–Sn–Cl(3)	94.7(1)	O(2)–C(2)–C(4)	125.7(4)
Cl(2)–Sn–Cl(4)	95.1(1)	O(3)–C(6)–C(7)	106.9(4)
Cl(2)–Sn–O(1)	168.3(1)	O(3)–C(1)–C(3)	114.8(4)
Cl(2)–Sn–O(2)	91.9(1)	O(4)–C(2)–C(4)	114.2(4)
Cl(3)–Sn–Cl(4)	167.0(1)	O(4)–C(8)–C(9)	107.1(5)
Cl(3)–Sn–O(1)	86.1(1)	C(1)–O(3)–C(6)	118.3(4)
Cl(3)–Sn–O(2)	87.0(1)	C(1)–C(3)–C(5)	114.8(4)
Cl(4)–Sn–O(1)	82.6(1)	C(2)–O(4)–C(8)	118.6(4)
Cl(4)–Sn–O(2)	84.2(1)	C(2)–C(4)–C(5)	116.1(4)
O(1)–Sn–O(2)	76.5(1)	C(3)–C(5)–C(4)	113.3(4)
Sn–O(1)–C(1)–O(3)	179.3(5)	Sn'–O(2)–C(2)–O(4)	170.7(5)
Sn–O(1)–C(1)–C(3)	–2.7(6)	Sn'–O(2)–C(2)–C(4)	–11.4(6)
O(1)–C(1)–O(3)–C(6)	–0.4(6)	O(2)–C(2)–O(4)–C(8)	–0.3(6)
O(1)–C(1)–C(3)–C(5)	151.6(6)	O(2)–C(2)–C(4)–C(5)	156.8(5)
C(1)–O(3)–C(6)–C(7)	165.0(6)	C(2)–O(4)–C(8)–C(9)	–151.0(6)
C(3)–C(1)–O(3)–C(6)	–178.6(6)	C(8)–O(4)–C(2)–C(4)	–178.4(5)
O(3)–C(1)–C(3)–C(5)	–30.3(6)	O(4)–C(2)–C(4)–C(5)	–25.2(6)
C(1)–C(3)–C(5)–C(4)	–63.7(6)	C(2)–C(4)–C(5)–C(3)	–62.7(5)

Primed atoms are related to unprimed ones by $-x, -y, -z$.

**Fig. 2** Structure and numbering scheme of *cis*-[SnCl₄(H₂O)₂].C₃H₆(CO₂Et)₂

rather an unexpected result. Moisture leaked into the crystallization vessel because the solvent had washed out the grease on the stopper. The crystallization process was accelerated by opening the vessel for *ca.* 1 h to facilitate the penetration of moisture.

The new species **2** is well soluble in halogenated hydrocarbons but insoluble in aromatic and aliphatic hydrocarbons. Its crystals consist of *cis*-[SnCl₄(H₂O)₂] and C₃H₆(CO₂Et)₂ molecules in a 1:1 molar ratio (Fig. 2). In *cis*-[SnCl₄(H₂O)₂] the tin atom has a distorted-octahedral environment formed by four chlorine atoms and two *cis*-coordinated oxygen atoms from two water molecules. The molecule as a whole lies on the mirror plane passing through atoms Sn, Cl(2), Cl(3), O(1) and O(2). The Sn–Cl(1), Sn–Cl(2) and Sn–Cl(3) bond distances of 2.381(1), 2.361(2) and 2.361(2) Å (Table 2) as well as the interbond angles lie within the ranges observed for other [SnCl₄L₂] complexes.^{8–10} The Sn–O(1) and Sn–O(2) bond lengths are 2.138(5) and 2.124(4) Å. The bond distances and angles are similar to those in *cis*-[SnCl₄(H₂O)₂].3H₂O⁷ (for which a considerably high residual *R* was obtained). The present diester molecule lies on the two-fold axis passing through atom C(1). The C(3)–O(3) carbonyl bond distance is 1.224(5) Å. This bond is situated in the preferred synperiplanar conformation to the O(4)–C(4) bond. The two planar CO₂ groups form an angle of 28.3°. Each *cis*-[SnCl₄(H₂O)₂] molecule is linked to the diester through the hydrogen bond O(2)–HO(2)⋯O(3). The O(2)⋯O(3) distance is 2.671(4) Å.

Conclusion

Complex **1** was investigated in order to elucidate whether the number of atoms in the ring formed by the chelate ester ligand with the metal atom has an influence on the geometry around the latter. It was found that in complexes of TiCl₄ with C₂O₄(CH₂CH₂Ph)₂, CH₂(CO₂Et)₂ and C₂H₄(CO₂CH₂-CH₂Ph) the titanium atom is always octahedrally co-ordinated by four chlorine atoms and two carbonyl oxygen atoms of the

Table 2 Interatomic bond distances (Å), angles and torsion (°) angles with e.s.d.s in parentheses for complex **2**

Sn-Cl(1)	2.381(1)	C(1)-C(2)	1.523(6)
Sn-Cl(2)	2.361(2)	C(2)-C(3)	1.493(6)
Sn-Cl(3)	2.361(2)	C(3)-O(3)	1.224(5)
Sn-O(1)	2.138(5)	C(3)-O(4)	1.313(5)
Sn-O(2)	2.124(4)	O(4)-C(4)	1.467(5)
		C(4)-C(5)	1.493(6)
Cl(1)-Sn-Cl(2)	96.0(1)	Cl(3)-Sn-O(2)	91.4(2)
Cl(1)-Sn-Cl(3)	95.8(1)	O(1)-Sn-O(2)	82.4(2)
Cl(1)-Sn-O(1)	83.5(2)	C(1)-C(2)-C(3)	116.8(4)
Cl(1)-Sn-O(2)	83.0(2)	C(2)-C(3)-O(3)	121.9(4)
Cl(2)-Sn-Cl(3)	98.0(1)	C(2)-C(3)-O(4)	115.2(4)
Cl(2)-Sn-O(1)	88.3(2)	O(3)-C(3)-O(4)	123.0(4)
Cl(2)-Sn-O(2)	170.7(2)	C(3)-O(4)-C(4)	116.8(4)
Cl(3)-Sn-O(1)	173.7(2)	O(4)-C(4)-C(5)	107.8(4)
C(2')-C(1)-C(2)-C(3)	-172.7(6)	C(2)-C(3)-O(4)-C(4)	-50.3(4)
C(1)-C(2)-C(3)-O(3)	-74.3(5)	O(3)-C(3)-O(4)-C(4)	-1.4(1)
C(1)-C(2)-C(3)-O(4)	10.8(6)	C(3)-O(4)-C(4)-C(5)	170.2(5)

Primed atoms are related to unprimed ones by $\frac{z}{2} - x, y, 1 - z$.

Table 3 Crystal data and structure refinement details for complexes **1** and **2**

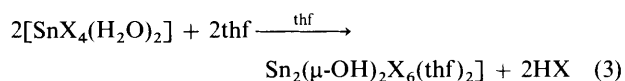
	1	2
Empirical formula	C ₂₀ H ₃₆ Cl ₁₂ O ₈ Sn ₂	C ₉ H ₂₀ Cl ₄ O ₆ Sn
<i>M</i>	1067.27	484.74
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>Pca</i> 2 ₁
<i>a</i> /Å	9.611(4)	9.335(4)
<i>b</i> /Å	10.413(5)	11.140(5)
<i>c</i> /Å	10.369(8)	17.490(7)
α /°	75.40(5)	
β /°	87.68(5)	
γ /°	78.73(4)	
<i>U</i> /Å ³	984(2)	1818(2)
<i>Z</i>	1	4
<i>D</i> _c /g cm ⁻³	1.800(2)	1.770(1)
<i>D</i> _m /g cm ⁻³	1.783	1.751
μ /mm ⁻¹	2.12	2.01
<i>F</i> (000)	524	960
Reflections collected	2426	1883
<i>hkl</i> ranges	0-9, -10 to -11, -11 to -11	0-9, 0-14, 0-22
Unique reflections	1963	1090
Goodness-of-fit on <i>F</i> ²	1.091	1.086
Final <i>R</i> ₁ ^a	0.0238	0.0266
<i>wR</i> ₂ ^b	0.0599	0.0670

^a $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$. ^b $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

diester molecule. In these complexes the chelate ester ligands and titanium form five-,³ six- and seven-membered rings, respectively.¹¹ However, the reaction of MgCl₂ with diethyl succinate gives the ionic compound [Mg{C₂H₄(CO₂Et)₂]₃·[MgCl₄]₂·2CH₂Cl₂.¹² The crystal structure of the [Mg{C₂H₄(CO₂Et)₂]₃²⁺ cation consists of [Mg{C₂H₄(CO₂Et)₂]₂²⁺ units linked by other diethyl succinate molecules to create a linear polymer. Diethyl glutarate, which has one more CH₂ group between carbonyl groups than diethyl succinate, gives with SnCl₄ the dimeric compound **1** in which a sixteen-membered ring is formed by two Sn atoms and by two C₃H₆(CO₂Et)₂ ligands. A similar dimeric complex [Ti₂Cl₈{ μ -*m*-C₆H₄(CO₂Et)₂]₂ has been obtained in the reaction of diethyl *m*-phthalate with TiCl₄.^{4,5} It follows the eight-membered ring species which could be formed between a metal atom and diethyl glutarate is unstable.

Unexpectedly, a monomeric complex, *cis*-[SnCl₄(H₂O)₂]₂·C₃H₆(CO₂Et)₂, was isolated from the filtrate of reaction (2). It is well known that the reaction of SnCl₄ with a trace of water in tetrahydrofuran results in the formation of dimeric tin(IV) complexes [Sn₂(μ -OH)₂X₆(thf)₂]₂·2thf (X = Br¹³ or Cl¹⁴; thf = tetrahydrofuran) with further substitution of X not being

observed [equation (3)]. It seems that *cis*-[SnCl₄(H₂O)₂] is the



intermediate leading to dimeric hydroxide-bridged tin(IV) complexes, which are exceptionally stable [reaction (3)]. The side-product HX reacts further with thf¹⁵ and causes the reaction equilibrium to shift towards the formation of [Sn₂(μ -OH)₂X₆(thf)₂]. Dichloromethane does not react with HX and the equilibrium (3) is shifted to the left. Therefore compound **2** is stable in CH₂Cl₂.

Experimental

All manipulations were carried out under dinitrogen by use of standard Schlenk and vacuum-line techniques. The anhydrous SnCl₄ was of commercial grade. The diester C₃H₆(CO₂Et)₂ was obtained by a standard procedure, *viz.* reaction of glutaric acid with ethyl alcohol.¹⁶ Solvents were dried and purified by standard techniques. Infrared spectra were obtained using a Perkin-Elmer 180 spectrometer.

Table 4 Final atomic coordinates with e.s.d.s in parentheses for non-hydrogen atoms of complex **1**

Atom	x	y	z
Sn	0.061 89(3)	0.174 58(3)	0.196 89(2)
Cl(1)	0.203 64(13)	0.338 12(11)	0.105 48(10)
Cl(2)	0.201 11(12)	0.055 52(10)	0.388 88(9)
Cl(3)	0.168 93(11)	0.027 25(10)	0.063 15(9)
Cl(4)	-0.091 75(13)	0.318 82(10)	0.305 76(9)
Cl(5)	0.324 13(13)	-0.542 53(13)	0.528 78(12)
Cl(6)	0.519 87(18)	-0.738 99(15)	0.421 70(16)
O(1)	-0.097 7(4)	0.258 6(3)	0.037 70(24)
O(2)	0.094 5(3)	-0.046 4(3)	-0.250 7(3)
O(3)	-0.229 5(3)	0.346 3(3)	-0.143 7(3)
O(4)	0.221 7(3)	0.114 8(3)	-0.293 7(3)
C(1)	-0.105 4(5)	0.307 9(4)	-0.085 1(4)
C(2)	0.099 4(5)	0.075 6(4)	-0.287 2(4)
C(3)	0.015 7(6)	0.332 4(5)	-0.174 4(4)
C(4)	-0.024 2(5)	0.187 8(5)	-0.330 8(4)
C(5)	-0.006 5(6)	0.326 9(5)	-0.318 7(4)
C(6)	-0.355 6(5)	0.328 6(6)	-0.061 8(5)
C(7)	-0.481 6(6)	0.413 1(7)	-0.144 3(6)
C(8)	0.350 9(6)	0.011 8(6)	-0.256 4(6)
C(9)	0.454 4(7)	0.076 3(7)	-0.204 4(6)
C(10)	0.341 3(7)	-0.660 6(6)	0.431 5(6)

Table 5 Final atomic coordinates with e.s.d.s in parentheses for non-hydrogen atoms of complex **2**

Atom	x	y	z
Sn	0.954 53(5)	0.214 22(4)	0.25
Cl(1)	0.932 94(12)	0.186 17(9)	0.384 45(6)
Cl(2)	0.888 75(20)	0.418 83(13)	0.25
Cl(3)	1.205 56(20)	0.240 44(18)	0.25
O(1)	0.731 7(6)	0.169 8(5)	0.25
O(2)	0.977 3(7)	0.024 5(4)	0.25
O(3)	0.973 5(4)	0.144 9(3)	0.645 18(17)
O(4)	1.022 0(4)	0.310 5(3)	0.578 51(17)
C(1)	1.25	0.213 7(6)	0.50
C(2)	1.155 1(6)	0.134 9(4)	0.550 0(3)
C(3)	1.042 5(5)	0.197 2(4)	0.595 86(23)
C(4)	0.909 9(6)	0.374 2(4)	0.621 1(3)
C(5)	0.896 2(7)	0.497 0(5)	0.587 9(3)

Synthesis of octachlorodi- μ -(diethyl glutarate-*O, O'*)-ditin(IV)-dichloromethane(1/2) **1**

To SnCl₄ (1 cm³, 2.2 g, 8.5 mmol) in CH₂Cl₂ (50 cm³), diethyl glutarate (1.6 cm³, 8.7 mmol) was added dropwise. The colourless solution was stirred for 1 h at room temperature and then filtered. The volume was reduced under vacuum to 30 cm³ and left to crystallize at 270 K. After 24 h the colourless prism-shaped crystals were filtered off and washed with hexane (3 × 5 cm³). Yield 3.4 g (75.0%) (Found: Cl, 30.7; Sn, 25.4. Calc. for C₉H₁₆Cl₄O₄Sn: Cl, 31.6; Sn, 26.5%).

Synthesis of diaquatetrachlorotin(IV)-diethyl glutarate (1/1) **2**

A solution of compound **1** (2.5 g, 2.3 mmol) in dichloromethane (50 cm³) was stirred at room temperature for 2 h then filtered and left to crystallize at 270 K. After 2 d the colourless crystals of **1** were filtered off and the filtrate was concentrated under vacuum to 20 cm³ and left for further crystallization. After 2 months a small amount of colourless, needle-shaped crystals were formed. These were identified by X-ray diffraction as *cis*-[SnCl₄(H₂O)₂]₂·C₃H₆(CO₂Et)₂.

Crystallography

Intensities were collected at 150.0(5) K using a Kuma KM4 four-circle diffractometer in the ω -2 θ mode (with crystals of dimensions 0.3 × 0.3 × 0.3 for **1** and 0.5 × 0.5 × 0.4 mm for **2**) and Mo-K α radiation (λ 0.710 71 Å) using an Oxford

System Cryostream Cooler. The crystals were cut from large crystals. For both complexes the intensities of three standard reflections, monitored every 100 intensity scans, showed no evidence of crystal decay. Of the 2426 ($4 < 2\theta < 56^\circ$) and 1883 ($4 < 2\theta < 46^\circ$) reflections measured for **1** and **2**, respectively, 1963 and 1090 unique reflections with $I > 3.0\sigma(I)$ were used for calculations.

The structures were solved by the Patterson method and refined by full-matrix least-squares calculations using SHELXL 93.¹⁷ The number of refined parameters was 244 for **1** and 129 for **2**. Neutral atom scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 18; real and imaginary components of anomalous dispersion were included for all non-H atoms. The hydrogen atoms were localized from Fourier-difference syntheses and their positional parameters were fully refined. Absorption corrections following the DIFABS¹⁹ procedure were applied: minimum and maximum 0.944 and 1.037 for **1** and 0.938 and 1.039 for **2**. Weighting schemes of the form $w = 1/[\sigma^2(F_o^2) + (0.0300P)^2 + 2.01P]$ and $1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.00P]$ [$P = (F_o^2 + 2F_c^2)/3$] were applied for **1** and **2**, respectively. Final $R_1(F)$ and $wR_2(F^2)$ values were 0.0238 and 0.0599 for **1** and 0.0266 and 0.0670 for complex **2**. For the last cycle of the refinement the maximum value of the ratio Δ/σ was $< 0.005 \text{ \AA}$ for **1** and **2**. The final difference map showed a general background within -0.65 and 0.42 for **1** and -0.64 and 0.65 e \AA^{-3} for **2**. A summary of the crystal data and refinement parameters is given in Table 3, final positional parameters for the non-hydrogen atoms in Tables 4 and 5.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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