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Synthesis and characterisation of tin(II) and tin(IV) citrates

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A series of tin(II) citrates, $SnM(C_6H_4O_7)$ (M = Sn or Zn) and $SnMM'(C_6H_4O_7)$ (M = M′ = Na, K or NH_4; M = NMe_4, M′ = H) and related monotin(II) salts of 1,5-dimethyl and 1,5-di-*n*-butyl citrate have been synthesized and characterised by spectroscopic methods (IR, ^1H, ^{13}C, ^{119}Sn NMR, ^{119}Sn Mössbauer). The crystal structures of dimeric tin(II) 1,5-dimethyl citrate and an oxidation product, $Sn(NMe_4)_2(C_6H_5O_7)_2 \cdot 3.5H_2O$, have also been determined.

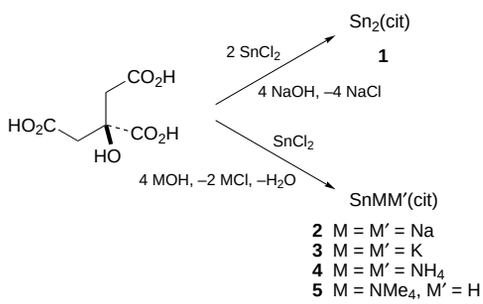
The citrate ion (3-carboxy-3-hydroxypentane-1,5-dioate) is ubiquitous in nature and is a key constituent of the tricarboxylic acid ('citric acid') cycle.[1] It is found in many fruits (oranges, lemons, currants, beetroots, *etc.*), fruit drinks and pharmaceutical syrups as well as being used to adjust the pH of food products. Numerous metal complexes of this potentially tetradentate ligand have been prepared.[2–6] Of particular importance is the interaction of tin with citric acid (H_4cit), as its use as a packaging material brings the two materials into intimate contact in many everyday products. The corrosion rates for tin and tin–iron alloys in the presence of fruit acids have been measured electrochemically[7–9] and the stability constant for $[SnMe_2]^{2+}$ with the citrate ion has been reported.[10] Surprisingly, however, definitive synthetic and structural studies of tin citrates are still lacking. The only compounds we have been able to find reported previously are Sn_2(cit) and Na_2Sn(cit),[11] the latter acting as an effective fruit juice stabiliser when storing juice in cans. pH Titrations have been used to show that Sn^{II} forms stable chelates of unresolved structure with citric acid and tentative claims have been made for the existence of '$[Sn(H_2cit)]_2O$' as the precipitate which forms from solutions of the tin(II) ion and a four-fold excess of citric acid.[12] The same report provides evidence for the existence of 1:1:1 $Sn^{2+}:M^{2+}:cit^{4-}$ (M = Cu or Fe) chelates. No structural studies have been made in this general area of tin chemistry, save for an extended X-ray absorption fine structure (EXAFS) investigation of $[\{Sn(cit)\}_4Pt\{\mu\text{-}Sn(cit)\}_2Pt\{Sn(cit)\}_4]^{6-}$ which failed to establish the connectivity between tin and the citrate ions.[13]

Our interest in this area stems from the application of tin(II) species in dental formulations, where the metal, originally incorporated as SnF_2 simply as a fluoride ion source, is now known to be orally active (antimicrobial) in its own right.[14] Citrate has long been a component of dental formulations and zinc citrate (ZCT) is still found in many toothpastes. In order to understand more fully the nature of Sn^{II}–H_4cit chemistry we have synthesized several new complexes containing both these components (including tin in both its oxidation states) and report the first crystallographic evidence for the bonding in such species.

Results and Discussion

Synthesis

Ditin(II) citrate **1** has been prepared from citric acid and tin(II) chloride (1:2) in the presence of 4 equivalents of base (Scheme 1). Similarly, salts of formula $SnMM'(C_6H_4O_7)$ have been prepared in the same way using equimolar quantities of the two principal reagents. The formation of compound **5** is somewhat surprising as the method of preparation followed exactly that

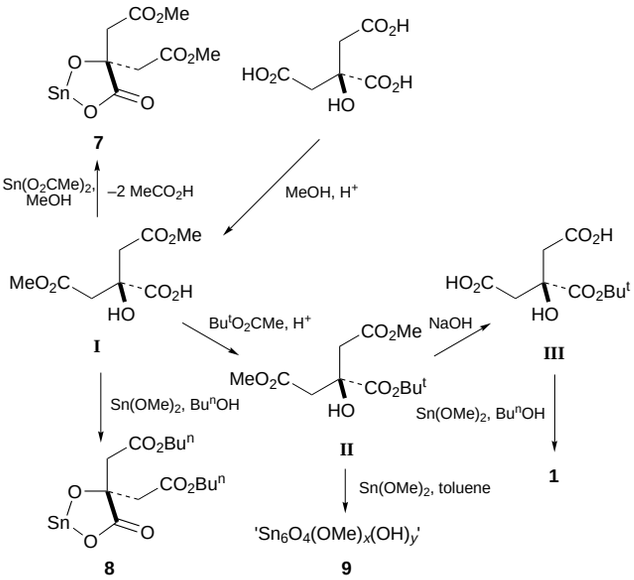


Scheme 1

used to synthesize **4**. The origin of the difference is unclear, though only **5** was crystallised from an organic solvent (methanol), which was also ultimately incorporated into the final product. A heterobimetallic species, SnZn(cit) **6**, has also been prepared, from **4** and $ZnCl_2$. Compounds **1** and **6** are both insoluble in all common solvents (**6** is sparingly soluble in boiling water) and are both probably polymeric in character.

In order to produce more soluble tin(II) citrates for spectroscopy/crystallisation purposes, we have attempted the synthesis of a number of tin(II) salts of selectively esterified citric acid. In addition to introducing solubilising ester groups, the reduced number of co-ordination sites on the ligand was also expected to induce solubility as well as a simplification of the co-ordination chemistry about the metal. In this way, the various co-ordinating sites of citric acid could be probed independently. The syntheses are summarised in Scheme 2.

1,5-Dimethyl,[15] 3-*tert*-butyl 1,5-dimethyl[16] and 3-*tert*-butyl citrates[16] **I**–**III** have been prepared by well documented procedures. Reaction of 1,5-dimethyl citrate with $Sn(O_2CMe)_2$ in methanol yields the monotin(II) complex **7** as its methanol adduct. Attempts to prepare **7** from soluble $Sn(OBu^n)_2$,[17] generated *in situ* from $Sn(OMe)_2$ in an excess of butanol, yielded the transesterification product **8**, although **7** is reformed on recrystallisation of **8** from methanol. Syntheses involving the triester **II** as a bulky alcohol were not successful, in as much as reaction with $Sn(OMe)_2$ in toluene yielded a crystalline material **9** with very low organic content. Microanalytical data (C, 3.70; H, 1.04%) lie between the theoretical values for $Sn_6O_4(OMe)_2(OH)_2$ (C, 2.75; H, 0.90%) and $Sn_6O_4(OMe)_3(OH)$ (C, 4.06; H, 1.14%). The species $Sn_6O_4(OMe)_4$ has been reported previously as the controlled hydrolysis product of $Sn(OMe)_2$ and shown to contain an $[Sn_6O_4]^{4+}$ adamantane core[18] and the product we have reproducibly isolated seems consistent with this class of compound, though unfortunately the crystals obtained were unsuitable for diffraction purposes. However, **9** and $Sn_6O_4(OMe)_4$ exhibit ν(Sn–O) at 547 and 570 cm^{-1}, respectively and



Scheme 2

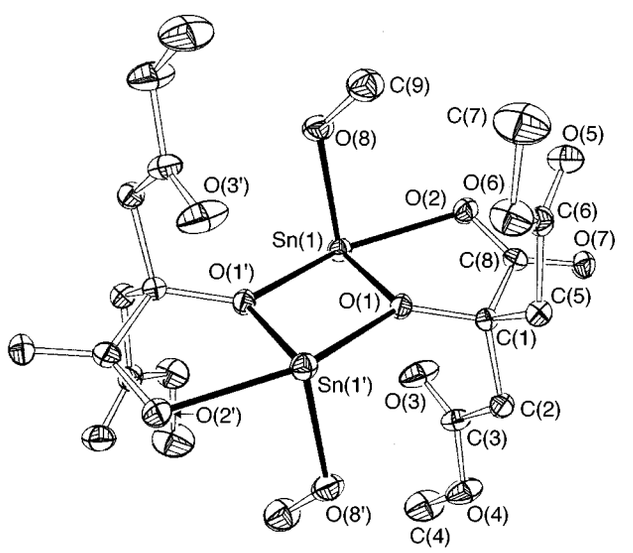


Fig. 1 The asymmetric unit of compound **7** showing the labelling scheme used in the text and tables. Primed atoms are related to their unprimed analogues by an inversion centre at the centre of the Sn_2O_2 ring. Thermal ellipsoids are at 30% probability

have similar Mössbauer isomer shift (i.s.) values (2.66 and 2.78 mm s^{-1}). Our intended target $Sn[OC(CH_2CO_2Me)_2(O_2CBu^t)]_2$, may well have been an intermediate in this reaction. The reaction of **III** with $Sn(OBu^n)_2$ (generated *in situ* as described above)[17] yielded an insoluble material which analysed for Sn_2(cit) **1**, rather than $Sn(O_2CCH_2)_2C(OH)CO_2Bu^t$ as hoped.

X-Ray crystallography

The asymmetric unit of tin(II) 1,5-dimethyl citrate **7** as its monomethanolate is shown in Fig. 1. Selected metric data are given in Table 1. The molecule adopts a dimeric structure in which each tin atom is located in a distorted trigonal bipyramidal pseudo-four-co-ordinate SnO_4E (E = lone pair) environment. Three of the four oxygens around the tin are due to the central carboxylate O(2) and the α-hydroxyl group O(1) from one dimethyl citrate ligand, together with oxygen from the co-ordinated methanol molecule O(8). The fourth oxygen is due to the α-hydroxyl oxygen of an adjacent molecule O(1′). The two halves of the dimeric unit are linked by an inversion centre (*i*) such that central Sn_2O_2 ring is constrained to be planar. Although the 1,5-dimethyl citrate ester was deliberately prepared in order

Table 1 Selected geometric data (bond lengths in Å, angles in °) for compound **7**

O(1′)–Sn(1)	2.393(5)	O(2)–Sn(1)	2.266(5)
O(8)–Sn(1)	2.272(6)	Sn(1)–O(1)	2.094(5)
C(1)–O(1)	1.416(6)	C(8)–O(2)	1.265(7)
C(3)–O(3)	1.198(7)	C(3)–O(4)	1.337(7)
C(4)–O(4)	1.457(7)	C(6)–O(5)	1.194(7)
C(6)–O(6)	1.339(7)	C(7)–O(6)	1.450(8)
C(8)–O(7)	1.237(7)	C(9)–O(8)	1.416(7)
H(8)–O(8)	0.960(2)		
O(2)–Sn(1)–O(1′)	137.4(1)	O(8)–Sn(1)–O(1)	95.5(2)
O(8)–Sn(1)–O(2)	84.4(2)	O(2)–Sn(1)–O(1)	73.3(2)
O(1)–Sn(1)–O(1′)	67.3(1)	O(1′)–Sn(1)–O(8)	83.7(2)
C(1)–O(1)–Sn(1′)	129.4(4)		

to exclude the terminal CH_2CO_2R groups from co-ordinating to the tin, chelation involving only the hydroxy and central carboxylate group has been observed elsewhere in non-esterified citrate compounds. For example, the antimony compounds $Sb_2Ag_2(H_2cit)_4$[19] and $SbM(H_2cit)_2(H_2O)_2\cdot H_2O$ (M = Li, Na or K)[3,19] have been found to contain divalent citrate anions which co-ordinate exclusively through the central carboxylate and the α-hydroxyl group. The carbonyl group incorporating O(3′), which approaches Sn(1) from above the Sn_2O_2 plane at a distance of only 2.787 Å, could be construed as expanding the co-ordination sphere about tin to SnO_5E, but the strength of the C(3)–O(3) bond [1.198(7) Å], which is comparable to that of unco-ordinated C(6)–O(5) [1.194(7) Å] and shorter than the hydrogen-bonded C(8)–O(7) [1.237(7) Å] (see below), suggests otherwise.

The strongest of the Sn–O bonds involves the alkoxide O(1) [Sn(1)–O(1) 2.094(5) Å], while the intermolecular Sn(1)–O(1′) [2.393(5) Å] is somewhat weaker, though both lengths are comparable with the bonds in dimeric $Sn(OBu^t)_2$ [1.97(2)–2.16(1) Å].[20] The bond to the monodentate carboxylate group [Sn(1)–O(2) 2.266(5) Å] is intermediate between the extremes found in compounds such as $Sn(O_2CH)_2$ which contain bidentate ligands (2.14–2.36 Å).[21] The Sn–O(H)CH_3 interaction [2.272(6) Å] is in the middle of the range for such solvates (2.117–2.404 Å).[22,23]

The lattice structure of compound **7** is built around hydrogen bonds linking H(8) [attached to O(8) of the co-ordinated methanol] and the non-bonded oxygen from the central carboxylate O(7), as shown in Fig. 2. Atom H(8) was located [O(8)–H(8) 0.960(2) Å] and the length and linearity of the hydrogen bond [H(8)···O(7) 1.63 Å, O(8)–H(8)–O(7) 166.8°] reflects its strength. The non-bonded distance O(7)–O(8) is 2.577 Å.

When an aqueous solution of compound **5** was allowed to evaporate over several weeks under aerobic conditions a viscous oil formed which partially crystallised on standing. Several crystals were hand-picked, washed with diethyl ether and found by X-ray crystallography to be the oxidation product $[NMe_4^+]_2$-$[Sn(Hcit)_2^{2-}]\cdot 3.5H_2O$ **10**. The quality of this structure determination is low, but is of sufficient quality to unequivocally identify the basic structural units and their interactions. The asymmetric unit (Fig. 3) consists of two molecules which are essentially identical within the limitations of the data set. Selected metric data are given in Table 2. Only the co-ordination about Sn(1) will be discussed. This consists of a distorted octahedral SnO_6 arrangement from the bonding of two [$Hcit^{3-}$] ligands to the tin, the charge balance being achieved by the two quaternary ammonium cations. The dianion adopts a *fac* rather than a *mer* isomeric form, in which the deprotonated α-hydroxy groups are *trans* to each other [O(3)–Sn(1)–O(1) 178.4(5)°]. The remaining CO_2^- and $CH_2CO_2^-$ groups are mutually *cis*, while one methylene carboxylate group remains protonated and uninvolved in metal binding. Other compounds which contain

Table 2 Selected geometric data (bond lengths in Å, angles in °) for compound **10**

O(1)–Sn(1)	2.10(1)	O(3)–Sn(1)	2.07(2)
O(6)–Sn(1)	2.13(1)	O(8)–Sn(1)	2.07(1)
O(10)–Sn(1)	1.96(2)	O(11)–Sn(1)	2.12(2)
C(1)–O(1)	1.11(2)	C(12)–O(14)	1.20(3)
C(1)–O(2)	1.21(2)	C(3)–O(3)	1.32(3)
C(5)–O(4)	1.20(3)	C(5)–O(5)	1.35(3)
C(6)–O(6)	1.19(3)	C(6)–O(7)	1.28(2)
C(7)–O(8)	1.29(2)	C(7)–O(9)	1.20(2)
C(9)–O(10)	1.41(3)	C(10)–O(11)	1.38(2)
C(10)–O(12)	1.19(2)	C(12)–O(13)	1.23(3)
O(15)–Sn(2)	2.04(2)	O(17)–Sn(2)	2.11(2)
O(17)–Sn(2)	1.89(2)	O(20)–Sn(2)	2.04(2)
O(22)–Sn(2)	2.06(3)	O(24)–Sn(2)	2.03(3)
C(13)–O(15)	1.56(3)	C(13)–O(16)	1.23(2)
C(15)–O(17)	1.59(4)	C(17)–O(18)	1.27(4)
C(17)–O(19)	1.30(4)	C(18)–O(20)	1.46(4)
C(18)–O(21)	1.19(3)	C(19)–O(22)	1.41(5)
C(19)–O(23)	1.32(4)	C(21)–O(24)	1.46(4)
C(23)–O(25)	1.45(3)	C(23)–O(26)	1.27(3)
C(24)–O(27)	1.15(4)	C(24)–O(28)	1.33(3)
O(3)–Sn(1)–O(1)	87.1(6)	O(6)–Sn(1)–O(1)	86.3(5)
O(6)–Sn(1)–O(3)	79.4(6)	O(8)–Sn(1)–O(1)	93.8(5)
O(8)–Sn(1)–O(3)	91.6(6)	O(8)–Sn(1)–O(6)	171.0(6)
O(10)–Sn(1)–O(1)	92.5(7)	O(10)–Sn(1)–O(3)	178.4(5)
O(10)–Sn(1)–O(6)	99.0(7)	O(10)–Sn(1)–O(8)	90.0(7)
O(11)–Sn(1)–O(1)	173.8(5)	O(11)–Sn(1)–O(3)	98.4(6)
O(11)–Sn(1)–O(6)	91.9(6)	O(11)–Sn(1)–O(8)	89.0(6)
O(11)–Sn(1)–O(10)	81.9(7)	O(17)–Sn(2)–O(15)	92.8(9)
O(20)–Sn(2)–O(15)	89.5(8)	O(20)–Sn(2)–O(17)	84.9(9)
O(22)–Sn(2)–O(15)	92.1(10)	O(22)–Sn(2)–O(17)	87.1(11)
O(22)–Sn(2)–O(20)	171.9(10)	O(24)–Sn(2)–O(15)	91.3(10)
O(24)–Sn(2)–O(17)	175.7(8)	O(24)–Sn(2)–O(20)	96.3(9)
O(24)–Sn(2)–O(22)	91.7(11)	O(27)–Sn(2)–O(15)	171.5(9)
O(27)–Sn(2)–O(17)	94.2(9)	O(27)–Sn(2)–O(20)	95.8(9)
O(27)–Sn(2)–O(22)	83.6(10)	O(27)–Sn(2)–O(24)	81.6(10)

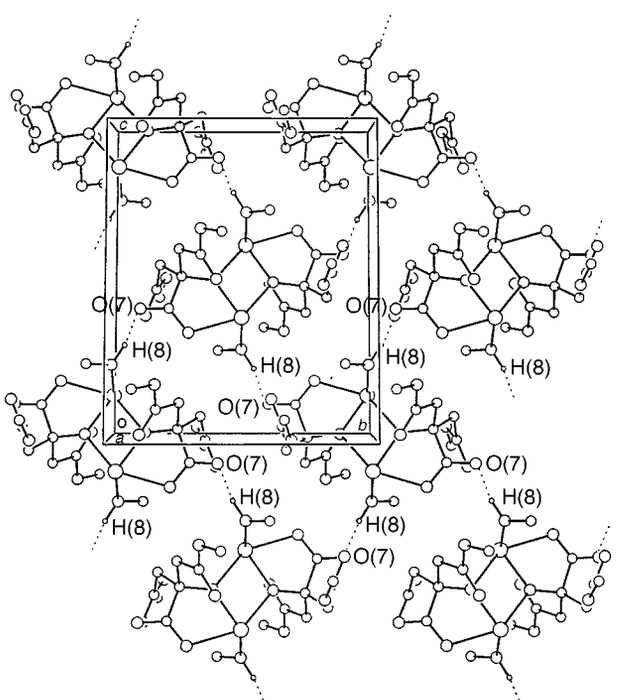


Fig. 2 The lattice structure of compound **7** viewed along *a*. Hydrogen bonds are shown as dotted lines

the same tridentate citrate bonding to the central metal are the anions $[M(Hcit)(H_2O)^-]$ (M = Mn^{2+} or Mg^{2+}).[24,25]

Of the Sn–O bonds, the ones to the α-hydroxy groups [Sn(1)–O(3) 2.07(2), Sn(1)–O(10) 1.96(2) Å] are shorter than those to the carboxylic acid groups [2.07(1)–2.13(1) Å], and in

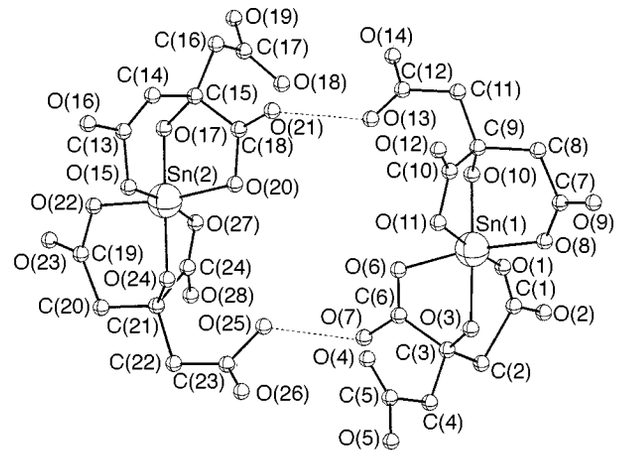


Fig. 3 The anionic part of the asymmetric unit (two molecules) of compound **10** showing the labelling scheme used in the text and tables. Hydrogen bonds are shown as dotted lines

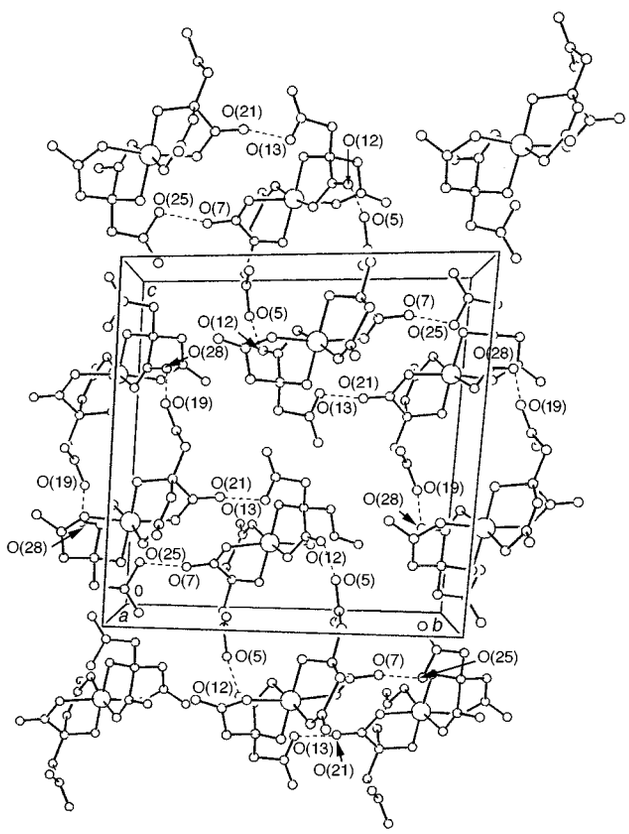


Fig. 4 The unit cell of compound **10** viewed along *a* showing hydrogen bonds between $[Sn(Hcit)_2]^{2-}$ units (dotted lines) only. The $[NMe_4]^+$ units and lattice water have been omitted for clarity

general all such bonds are shorter than in the tin(II) derivative **7** described earlier.

The lattice structure of compound **10** is a consequence of two hydrogen-bonded networks. The simplest of these involves the C=O and C–OH groups of the citrate ligands, with the non-co-ordinating oxygens of the central carboxylic acid groups [O(7), O(12) on Sn(1); O(21), O(28) on Sn(2)] interacting with the presumably protonated oxygens of the non-chelating methylene carboxylic acids [O(5), O(13) on Sn(1); O(19), O(25) on Sn(2)]. Thus, O(7) and O(13) hydrogen bond with O(25) and O(21) respectively (2.66, 2.61 Å), while O(12) is linked to O(5) generated by the operator $1 - x$, $1 - y$, $-z$ (2.57 Å). Atoms O(28) and O(19) (symmetry operator $1 - x$, $-y$, $1 - z$) behave similarly (2.67 Å). These features are illustrated in Fig. 4.

In addition, seven water molecules O(1′)–O(8′) [two included

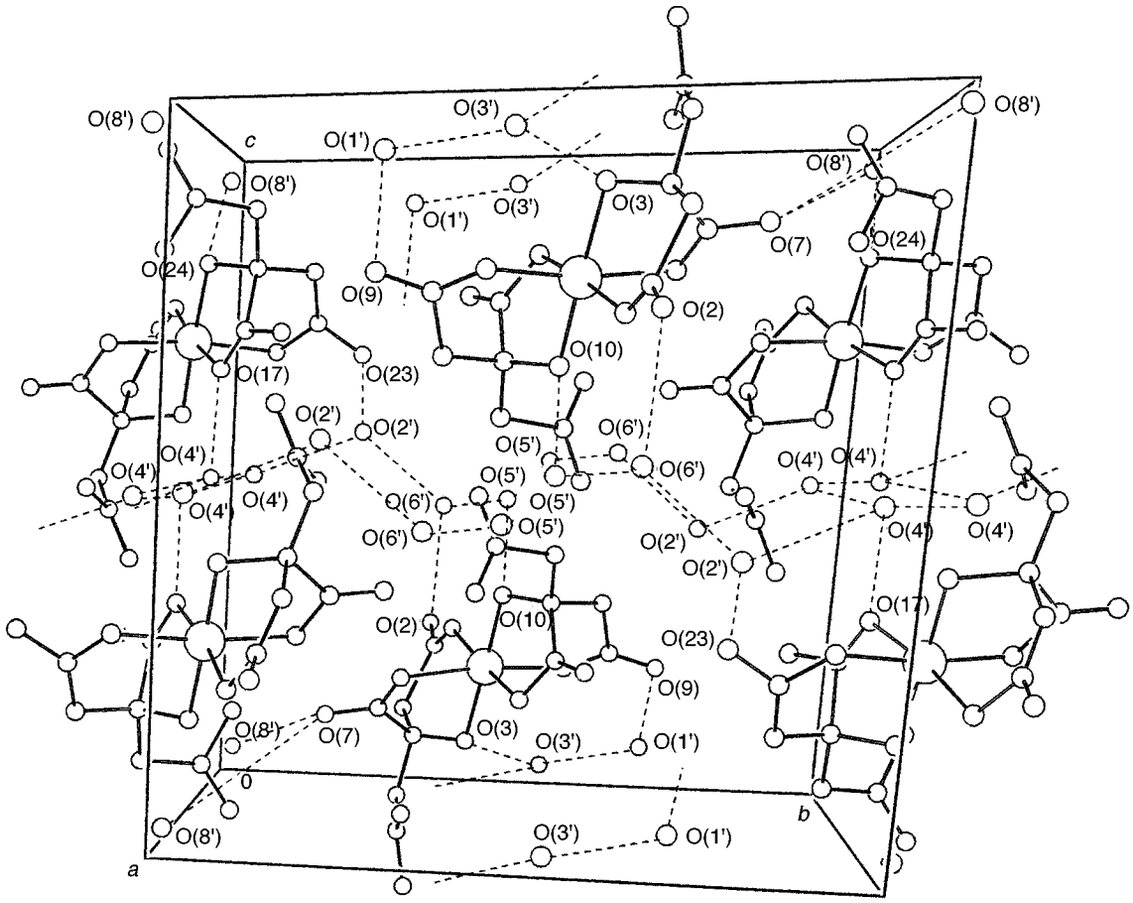


Fig. 5 The unit cell of compound **10** viewed along *a* showing hydrogen bonds involving water (dotted lines)

Table 3 Selected intermolecular interactions (Å) for compound **10**

Involving carboxylate groups only			
O(7)···O(25)	2.66	O(12)···O(5a)	2.57
O(13)···O(21)	2.61	O(28)···O(19b)	2.67
Involving water molecules			
O(1)···O(3′)	2.55	O(1′)···O(9′)	3.05
O(7)···O(1′c)	2.75	O(3′)···O(3′c)	2.72
O(4′)···O(2′)	2.93	O(4′)···O(17b)	2.78
O(2′)···O(23b)	2.68	O(4′)···O(4′d)	2.70
O(2′)···O(6′)	2.87	O(5′)···O(6′)	2.68
O(5′)···O(10)	2.88	O(8′)···O(24b)	2.80
O(8′)···O(7e)	2.65	O(6′)···O(2)	3.40
O(3)···O(3′)	2.78		

Key to symmetry operations relating designated atoms to reference atoms at *x*, *y*, *z*: a $1-x$, $1-y$, $-z$; b $1-x$, $-y$, $1-z$; c $-x$, $1-y$, $-z$; d $-x$, $-y$, $1-z$; e *x*, *y*, $1+z$.

at half occupancies, O(5′) and O(8′)] were refined and are linked in a complex fashion to each other and to the citrate ligands. The short contacts for each of these oxygens are given in Table 3, and shown in Fig. 5. The water molecules form (*i*) puckered sheets running through the centre of the unit cell parallel to *a* [O(2′), O(4′), O(5′), O(6′)], (*ii*) a symmetry-generated group of eight molecules based on O(1′) and O(3′) at the top and bottom centres of the cell and (*iii*) a group based solely on O(8′) in the cell corners. Effectively, water molecules fill the void space generated by the earlier hydrogen-bonded network.

Spectroscopy

The starting point for any discussion of the available spectroscopic data (Table 4) are the measurements relating to the two crystal structures. The Mössbauer and ^{119}Sn NMR data for compound **10** are unique in being the only data referring to a tin(IV) species. This is clearly reflected in the i.s. of 0.16 mm s^{-1}, while the quadrupole splitting (q.s.) of 1.36 mm s^{-1} arises from the asymmetric co-ordination (differing Sn–O bonds) about the tin. This environment is clearly more distorted than most SnO_6 octahedra, which have small or unresolved q.s. {*e.g.* tin(IV) site in $[Sn_2O(O_2CCF_3)_4O(OCF_3)_2]_2$, q.s. 0.52 mm s^{-1}}. A more reasonable parallel can be drawn with $Sn(O_2CCF_3)_4$ (q.s. 1.56 mm s^{-1}), which is believed to contain two bi- and two monodentate carboxylate groups.[26] In addition, two resonances in the ^{119}Sn NMR spectrum (δ −54.2, −55.3) suggest that the two non-equivalent tin sites present in the solid state are retained in solution, presumably through the C=O···HO hydrogen bonds.

The Mössbauer data for compound **7** (i.s. 3.11, q.s. 2.01 mm s^{-1}), particularly the i.s., are intermediate between values for the

Table 4 Spectroscopic data for tin citrates

Compound	i.s./mm s^{-1}	q.s./mm s^{-1}	δ (^{119}Sn)	$\nu_{asym}(CO_2)$
1	3.07	1.90	−724.9[a]	1553
2	3.06	1.85	−579.9	1593
3	2.97	1.81	−578.3	1599
4	2.99	1.84	−579.6	1599
5	2.80	1.91	−582.9	1616
6	3.17	1.92	—[b]	1567
7	3.11	2.01	−482.0	1561, 1734
8	3.13	1.98	−497.0	1543, 1740
10	0.16	1.36	−54.2, −55.3	1644, 1727
11	3.17	1.93	−494.1	1560
12	3.29	1.90	−489.8	1555
13	3.25	1.90	−480.6	1553

[a] Solid-state CP MAS data. [b] Insoluble in all common solvents.

homoleptic $Sn(OR)_2$ (R = Me 2.80, 2.02; Bu^n 2.87, 1.97 mm s^{-1})[17] and $Sn(O_2CR)_2$ (R = Me 3.31, 1.77 mm s^{-1})[27] in accordance with the heteroleptic nature of the co-ordination in this species. The co-ordination number of the simple tin(II) alkoxides cited above is, however, uncertain, but an SnO_4E co-ordination as in the carboxylates is likely. In solution, soluble oligomeric tin(II) alkoxides (R = Bu^n or Bu^t) display pseudo-three-co-ordinate SnO_3E stereochemistry and thus exhibit tin NMR chemical shifts significantly different to those of **7**, *e.g.* $[Sn(OBu^t)_2]_2$, δ(^{119}Sn) −93.6.[20] The ^{119}Sn NMR signal for **7** (δ −482.0) is, however, in line with data for simple soluble pseudo-four-co-ordinate carboxylates (SnO_4E) such as tin(II) laurate (**11**), palmitate (**12**) and stearate (**13**) (δ −494.1, −489.8, −480.6) which have been spectroscopically characterised for the first time as part of this study. Clearly, **8** is structurally similar to **7** given the overall similarity of the spectral data [δ(^{119}Sn) −497.0; i.s. 3.13, q.s. 1.98 mm s^{-1}], though both the analytical and spectroscopic data rule out co-ordinated alcohol. The microanalysis suggests the presence of water (probably from the butanol used in the reaction) which is more likely to generate a hydrogen-bonded lattice, similar to that of **10**, than is the bulkier butanol.

The IR data for compounds **7** and **10** are of interest since they provide reference points against which the bonding of the carboxylate groups in the remaining species can be judged. Both compounds contain unidentate carboxylate groups, though in both cases the carbonyl groups are involved in hydrogen bonding. Thus, for **7**, $\nu_{asym}(CO_2)$ at 1561 cm^{-1} represents a strongly hydrogen-bonded carboxylate, while for **10** $\nu_{asym}(CO_2)$ at 1644 cm^{-1}, though at higher wavenumber than might have been expected, is in accordance with the weak hydrogen-bonding present for at least some of the carbonyl groups [*e.g.* O(2), O(9), O(23), O(16)].

On the basis of the above, it seems reasonable that the monotin(II) species **2**–**5** all contain tin bound *via* the α-hydroxy and central CO_2 groups [i.s. 2.80–3.06, q.s. 1.81–1.91 mm s^{-1}; δ (^{119}Sn) −578.3 to −582.9] in which the tin-bound carboxylate group is essentially monodentate [$\nu_{asym}(CO_2Sn)$ 1593–1616 cm^{-1}]. The reaction of salicyclic acid and $Sn(OMe)_2$ is known to generate a product containing a related six-membered SnO_2C_2O heterocycle.[28] Thus, by analogy, Sn_2(cit) **1** also contains one tin in this environment, while the second tin is bound to the two bidentate methylene carboxylate groups [$\nu_{asym}(CO_2Sn)$ 1553 (br) cm^{-1}], presumably intermolecularly given the low solubility of the species. The two CH_2CO_2 moieties appear non-equivalent in the ^{13}C cross polarisation magic angle spinning (CP MAS) NMR spectrum of **1** (δ 48.8, 52.9) though the two tin environments must, however, be very similar as they only give rise to line broadening in both the Mössbauer and ^{119}Sn NMR spectra, rather than resolvable signals for each metal environment. It may be that the bonding in **1** is not as homogeneous as we have so far implied.

The heterobimetallic citrate **6**, which is formed in a stepwise manner from **4**, should contain tin in a similar environment to that present in **7** (q.s. 1.92 mm s^{-1}), while parallel comments can be made about the zinc co-ordination as for the second tin site in **1** [$\nu_{asym}(CO_2M)$: 1567v (br) cm^{-1}]. No structural data are available for Zn_2(cit) (a component of many contemporary toothpastes) due to its insolubility, but the structure of $Zn(H_2O)_3$(Hicit) (Hicit = 1-isopropyl citrate) has been determined.[29] In this species an octahedral ZnO_6 core is made up of ligation to the metal to three water molecules, the α-OH, the central and one terminal CO_2 groups.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (^{1}H, ^{13}C NMR), GX400 (^{119}Sn NMR), Perkin-Elmer 599B (IR). Details of our Mössbauer spectrometer and related procedures are given elsewhere.[30] For all compounds, infrared spectra were recorded as Nujol mulls on KBr plates and all NMR data were recorded on saturated solutions in D_2O at ambient temperature unless indicated otherwise. Tin(II) analyses were determined iodometrically.[31] Sodium and potassium analyses were determined by flame photometry. Zinc analysis was performed by atomic absorption spectrophotometry.

Syntheses

Ditin(II) citrate, $Sn_2(C_6H_4O_7)$ 1.[11] Anhydrous citric acid (2.11 g, 11.0 mmol) was dispersed in deoxygenated water (40 cm^3) with rapid stirring until fully dissolved. To this clear solution solid $SnCl_2$ (4.46 g, 23.5 mmol) was added and the mixture allowed to stir for 10 min until a clear solution was formed. 2 M Sodium hydroxide (20 cm^3) was added dropwise to the reaction mixture with stirring whilst also rapidly purging the flask with N_2. As the pH rose to 5.0 and above a dense white precipitate was formed. The solid product was rapidly filtered off and washed with successive aliquots of water, ethanol and diethyl ether. In order to remove the water held within the solid it was necessary to dry the solid *in vacuo* whilst warming to 70–80 °C. The product was a fine, white powder. Yield: 4.3 g (92%) [Found (Calc. for $C_6H_4O_7Sn_2$): C, 16.6 (16.9); H, 1.27 (1.65); Sn^{II}, 53.8 (55.8)%]. Selected infrared data (cm^{-1}): 1553s (br), ν_{asym}-(CO_2Sn); 489m (br), ν(Sn–O). ^{13}C CP MAS NMR data: δ 48.8 (CH_2), 52.9 (CH_2), 79.9 (tertiary C), 178.4 (CH_2CO_2Sn) and 181.3 (R_2CO_2Sn).

Disodium tin(II) citrate monohydrate, $Na_2Sn(C_6H_4O_7)\cdot H_2O$ 2.[11] Solid $SnCl_2$ (9.50 g, 50.1 mmol) was dissolved in deoxygenated water (25 cm^3). To this solution was slowly added 2 M NaOH (50 cm^3) whilst purging the flask with N_2. A dense white precipitate of hydrous tin(II) oxide was formed. This solid was rapidly filtered off, washed with water and immediately resuspended in deoxygenated water (25 cm^3). Anhydrous citric acid (9.60 g, 50.0 mmol) was added to this suspension and the mixture allowed to stir at room temperature for 10 min. Further 2 M NaOH (50 cm^3) was added dropwise to the reaction mixture until the slurry dispersed and a clear solution was formed. This solution was evaporated to dryness on a rotary evaporator yielding a colourless glass. The resulting solid was dispersed in Pr^iOH (20 cm^3), filtered and dried *in vacuo*. Yield: 11.9 g (96%) [Found (Calc. for $C_6H_6Na_2O_8Sn$): C, 19.9 (19.4); H, 1.90 (1.62); Na, 13.2 (12.4); Sn^{II}, 27.3 (32.0)%]. Selected infrared data (cm^{-1}): 3393s (br), ν(H–O–H); 1635m (sh), δ(H–O–H); 1593s (br), $\nu_{asym}(CO_2Sn)$; 500–575 (br), ν(Sn–O). ^{1}H NMR: δ 2.74 (q, 4 H, J = 15.3 Hz, CH_2). ^{13}C NMR: δ 46.7 (CH_2), 76.1 (tertiary C), 177.2 (CH_2CO_2Sn) and 183.7 (R_2CO_2Sn).

Hydrated dipotassium tin(II) citrate, $K_2Sn(C_6H_4O_7)\cdot 1.5H_2O$ 3. The preparation of compound **3** followed exactly the same procedure as for **2** with the exception that 2 M KOH solution was used in place of the 2 M NaOH. Yield: 91% [Found (Calc. for $C_6H_7K_2O_{8.5}Sn$): C, 17.6 (17.5); H, 1.73 (1.70); K, 17.9 (19.0); Sn^{II}, 26.3 (28.8)%]. Selected infrared data (cm^{-1}): 3373s (br), ν(H–O–H); 1650m (br), δ(H–O–H); 1599s (br), $\nu_{asym}(CO_2Sn)$; 480–500m (br), ν(Sn–O). ^{1}H NMR data: δ 2.78 (q, 4 H, J = 15.3 Hz, CH_2). ^{13}C NMR data: δ 47.2 (CH_2), 76.6 (tertiary C), 177.2 (CH_2CO_2Sn) and 184.4 (R_2CO_2Sn).

Hydrated diammonium tin(II) citrate, $(NH_4)_2Sn(C_6H_4O_7)\cdot 0.5H_2O$ 4. The preparation of compound **4** followed exactly the same procedure as for **2** with the exception that 2 M NH_4OH solution was used in place of the 2 M NaOH. Yield: 90% [Found (Calc. for $C_6H_{13}N_2O_{7.5}Sn$): C, 21.3 (20.5); H, 4.28 (3.73); N, 8.17 (7.95)%]. Selected infrared data (cm^{-1}): 3192w (br), ν(H–O–H); 1684w (br), δ(H–O–H); 1599s (br), $\nu_{asym}(CO_2Sn)$; 500–570 (br), ν(Sn–O). ^{1}H NMR data: δ 2.72 (q, 4 H, J = 15.4 Hz, CH_2) and 7.13 (br s, 8 H, NH_4). ^{13}C NMR: δ 46.3 (CH_2), 75.6 (tertiary C), 176.7 (CH_2CO_2Sn) and 183.7 (R_2CO_2Sn).

Tetramethylammonium tin(II) citrate methanol (1/2), $(NMe_4)HSn(C_6H_4O_7)\cdot 2MeOH$ 5. Solid $SnCl_2$ (4.75 g, 25.1 mmol) was dissolved in deoxygenated water (15 cm^3). To this clear solution 2 M NaOH (25 cm^3) was added dropwise whilst continuously purging the reaction flask with N_2. A dense white precipitate of hydrous tin(II) oxide was formed. This solid was rapidly filtered on a Schlenk-stick, washed with water and immediately resuspended in deoxygenated water (15 cm^3). Anhydrous citric acid (4.80 g, 25.0 mmol) was added and the mixture allowed to stir at room temperature for 10 min. Tetramethylammonium hydroxide pentahydrate (9.15 g, 51.0 mmol) was dissolved in deoxygenated water (25 cm^3) and the fresh solution was added dropwise to the reaction mixture until the slurry had dispersed and a completely clear solution had formed. This solution was evaporated to dryness on a rotary evaporator yielding a colourless, hygroscopic oil which was dissolved in methanol (20 cm^3) and allowed to precipitate overnight in a refrigerator. The product was filtered on a Schlenk-stick, washed with cold ether and dried *in vacuo*. Yield: 7.4 g (66%) [Found (Calc. for $C_{12}H_{26}NO_9Sn$: C, 32.5 (32.3); H, 5.61 (5.61); N, 3.57 (3.10); Sn^{II}, 25.4 (26.7)%]. Selected infrared data (cm^{-1}): 1616s (br), $\nu_{asym}(CO_2Sn)$; 567w (br), ν(Sn–O). ^1H NMR data: δ 2.73 (q, 4 H, $J = 15.1$ Hz, CH_2), 3.10 (s, 12 H, NCH_3) and 3.26 (s, 6 H, CH_3OH). ^{13}C NMR: δ 46.1 (CH_2), 48.4 (CH_3OH), 54.5, 54.7, 54.8 (NCH_3), 76.1 (tertiary C), 176.0 (CH_2CO_2Sn) and 183.4 (R_2CO_2Sn).

Hydrated tin(II) zinc citrate, $ZnSn(C_6H_4O_7)\cdot H_2O$ 6. Diammonium tin(II) citrate **4** (2.50 g, 7.3 mmol) was dissolved in deoxygenated water (25 cm^3), solid $ZnCl_2$ (0.99 g, 7.3 mmol) added and the mixture refluxed under N_2 for 12 h. After this time a dense white precipitate had formed around the inner surface of the flask. This solid was carefully suspended in the supernatant liquid, the resulting suspension allowed to cool to room temperature and methanol (5 cm^3) added to assist the precipitation. The product was filtered on a Schlenk-stick, washed with successive aliquots of water, ethanol and ether and thoroughly dried *in vacuo*. Yield: 2.1 g (77%) [Found (Calc. for $C_6H_4O_7SnZn$): C, 19.9 (19.4); H, 1.61 (1.08); Sn^{II}, 28.3 (31.8); Zn, 14.2 (17.6)%]. Selected infrared data (cm^{-1}): 3420w (br), ν(H–O–H); 1556–1579s, $\nu_{asym}(CO_2M)$; 500–557m (br), ν(M–O) (M = Sn or Zn). The NMR spectra were not recorded due to the poor solubility of the compound in common solvents.

1,5-Dimethyl citrate monohydrate, $(HO)C(CO_2H)(CH_2CO_2Me)_2\cdot H_2O$ I.[15] Anhydrous citric acid (50.0 g, 260.4 mmol) was dissolved in methanol (250 cm^3) together with 98% sulfuric acid (2.0 g). The mixture was refluxed for 1 h then allowed to cool to room temperature and cold water (250 cm^3) added with stirring. The solution was neutralised with solid calcium carbonate to remove the excess of citric and sulfuric acids as their insoluble calcium salts. The suspension was filtered and the filtrate evaporated to dryness *in vacuo*. This yielded a colourless glass which was redissolved in cold water (100 cm^3), filtered to remove traces of insoluble salts and the filtrate acidified to pH 4.5 with concentrated hydrochloric acid. The resulting white precipitate was filtered off, recrystallised twice from water and air-dried. Yield: 18.0 g (29%) [Found (Calc. for $C_8H_{14}O_8$): C, 40.6 (40.3); H, 5.97 (5.88)%]. M.p. 122 °C (lit.,[15] 125 °C). Selected infrared data (cm^{-1}): 3420s (sh), ν(H–O–H); 1742s (sh), $\nu_{asym}(CO_2H)$; 1717s (sh), $\nu_{asym}(Co_2Me)$; 1638m (br), δ(H–O–H); 1232m (sh), $\nu_{sym}(CO_2Me)$. ^1H NMR ($CDCl_3$): δ 2.87 (q, 4 H, $J = 15.4$ Hz, CH_2), 3.66 (s, 6 H, OCH_3) and 5.00 (br s, 2 H, H_2O). ^{13}C NMR: δ 43.9, 44.2 (CH_2), 52.2, 53.2 (OCH_3), 74.2 (tertiary C), 171.7, 171.8 ($CH_2CO_2CH_3$) and 176.4 (R_2CO_2H).

3-*tert*-Butyl 1,5-dimethyl citrate, $(HO)C[CO_2Bu^t](CH_2CO_2Me)_2$ II.[16] 1,5-Dimethyl citrate **I** (6.00 g, 25.2 mmol) was suspended in *tert*-butyl acetate (50 cm^3) and 60% perchloric acid (1.0 cm^3) solution carefully added. The mixture was stirred at room temperature for 72 h. After this time the reaction mixture was slowly poured into saturated sodium hydrogencarbonate solution (100 cm^3) and extracted with ether. This procedure was repeated twice (2 × 150 cm^3) and the combined ether extracts evaporated to dryness on a rotary evaporator. Light petroleum (b.p. 60–80 °C) (150 cm^3) was added to the residue and the oil dissolved with rapid stirring. The by-product of the reaction (trimethyl citrate) readily crystallises from this solution and can be efficiently removed by filtration. The clear filtrate was subsequently evaporated to yield the desired product as a colourless viscous oil. Yield: 5.4 g (78%) [Found (Calc. for $C_{12}H_{20}O_7$): C, 53.8 (52.2); H, 7.92 (7.30)%]. Selected infrared data (liquid film; cm^{-1}): 3489s (sh), ν(C–O–H); 1757s (sh), $\nu_{asym}(CO_2Bu^t)$, 1728s (sh), $\nu_{asym}(CO_2Me)$. ^1H NMR ($CDCl_3$): δ 1.51 [s, 9 H, $(CH_3)_3C$], 2.82 (q, 4 H, $J = 15.4$ Hz, CH_2) and 3.69 (s, 6 H, OCH_3). ^{13}C NMR: δ 27.5 [$(CH_3)_3C$], 43.2 (CH_2), 51.6 (OCH_3), 72.9 (tertiary C), 83.1 [$(CH_3)_3C$], 169.9 ($CH_2CO_2CH_3$) and 172.1 ($R_2CO_2Bu^t$).

3-*tert*-Butyl citrate, $(HO)C[CO_2Bu^t](CH_2CO_2H)_2$ III.[16] 3-*tert*-Butyl-1,5-dimethyl citrate **II** (5.00 g, 18.1 mmol) was dissolved in methanol (20 cm^3). 2 M Sodium hydroxide (20 cm^3) was slowly added to this solution and the mixture stirred at room temperature for 3 h. The solvent volume was then reduced by 50% on a rotary evaporator and the resulting aqueous solution acidified to pH 3 with concentrated hydrochloric acid. The product was extracted with ethyl acetate (3 × 100 cm^3), the extracts combined and the solvent removed *in vacuo* yielding a white solid product. The crude material was recrystallised from boiling ethyl acetate–hexane yielding a white, crystalline solid. Yield: 1.8 g (41%) [Found (Calc. for $C_{10}H_{16}O_7$): C, 48.2 (48.4); H, 6.50 (6.57)%]. M.p. 124 °C (lit.,[16] 124 °C). Selected infrared data (cm^{-1}): 3485m (sh), ν(O–H); 1755s (sh), $\nu_{asym}(CO_2Bu^t)$; 1705s (sh), $\nu_{asym}(CO_2H)$. ^1H NMR ($CDCl_3$): δ 1.41 (s, 9 H, CH_3) and 2.84 (q, 4 H, $J = 15.1$ Hz, CH_2). ^{13}C NMR: δ 26.5 [$(CH_3)_3C$], 43.0 (CH_2), 73.0 (tertiary C), 84.0 [$(CH_3)_3C$], 172.9 ($R_2CO_2Bu^t$) and 173.1 (CH_2CO_2H).

Tin(II) 1,5-dimethyl citrate methanol (1/1), $C[(O)CO_2Sn](CH_2CO_2Me)_2\cdot MeOH$ 7. 1,5-Dimethyl citrate **I** (250.0 mg, 1.1 mmol) was dissolved in deoxygenated, dry distilled methanol (25 cm^3). Tin(II) acetate (249.0 mg, 1.1 mmol) was carefully added with the exclusion of atmospheric oxygen. The reaction mixture was refluxed for 2 h under a nitrogen atmosphere. After this time a turbid off-white suspension remained which was filtered hot on a Schlenk-stick. The clear filtrate was allowed to cool slowly to room temperature where, upon standing, a mass of small colourless crystals precipitated which were filtered on a Schlenk-stick and washed with a little ice-cold ether. Yield: 0.36 g (89%) [Found (Calc. for $C_9H_{14}O_8Sn$): C, 27.6 (29.3); H, 3.53 (3.83)%]. Selected infrared data (cm^{-1}): 1734s (sh), $\nu_{asym}(CO_2Me)$; 1561s (br), $\nu_{asym}(CO_2Sn)$; 569m (sh), ν(Sn–O. ^1H NMR $[(CD_3)_2SO]$: δ 2.74 (q, 4 H, $J = 15.3$ Hz, CH_2), 3.38 (s, 3 H, CH_3OH) and 3.55 (s, 6 H, OCH_3). ^{13}C NMR: δ 45.2 (CH_2), 48.9 (CH_3OH), 51.3 (OCH_3), 75.7 (tertiary C), 172.0 (CH_2CO_2Me) and 182.0 (R_2CO_2Sn).

Attempted synthesis of tin(II) bis(3-*tert*-butyl 1,5-dimethyl citrate). 3-*tert*-Butyl 1,5-dimethyl citrate **II** (0.71 g, 2.6 mmol) was dissolved in freshly distilled toluene (10 cm^3) and added to tin(II) bis(methoxide) (0.23 g, 1.3 mmol). The resulting suspension was gently refluxed for 2 h yielding a slightly turbid solution. This was filtered hot on a Schlenk-stick and the clear filtrate allowed to stand overnight at room temperature. A mass of small, colourless crystals was formed which were filtered off and washed with a little ice-cold ethanol and ether. Yield: 0.11 g (12.7%). The product was tentatively identified as $Sn_6O_4(OMe)_3OH$ [Found (Calc. for $C_3H_{10}O_9Sn_6$): C, 3.7 (4.1); H, 1.04 (1.14)%]. Selected infrared data (cm^{-1}): 547s (br), ν(Sn–O).

Attempted synthesis of tin(II) 3-*tert*-butyl citrate. Tin(II) methoxide (0.15 g, 0.83 mmol) was dissolved in deoxygenated *n*-butanol (25 cm^3) with gentle warming. Solid 3-*tert*-butyl citrate **III** (0.21 g, 0.83 mmol) was added with stirring and the reaction mixture refluxed for 30 min. The suspension was allowed to cool to room temperature, the solid collected on a Schlenk-stick, washed with successive aliquots of ethanol and ether dried *in vacuo*. Yield: 0.09 g (44%). The product was identified as Sn_2(cit) **1** (Found: C, 16.9; H, 1.24%). Selected infrared data (cm^{-1}): 1553s (br), $\nu_{asym}(CO_2Sn)$, 494m (br), ν(Sn–O).

Tin(II) 1,5-di-*n*-butyl citrate $C[(O)CO_2Sn](CH_2CO_2Bu^n)_2\cdot H_2O$ 8. Tin(II) methoxide (0.38 g, 2.1 mmol) was dissolved in deoxygenated *n*-butanol (25 cm^3) with gentle warming. 1,5-Dimethyl citrate **I** (0.50 g, 2.1 mmol) was carefully added to the solution of soluble tin(II) *n*-butoxide and the reaction mixture gently refluxed for 30 min under an atmosphere of N_2. The resulting colourless solution was allowed to cool slowly to room temperature whereupon a fine, white precipitate was formed. The product was filtered on a Schlenk-stick and washed with ice-cold ether. Yield: 0.64 g (72%) [Found (Calc. for $C_{14}H_{24}O_8Sn$): C, 38.8 (38.3); H, 5.16 (5.52)%]. Selected infrared data (cm^{-1}): 3433, ν(H_2O); 1740s (sh), $\nu_{asym}(CO_2Bu^n)$; 1543s (br), $\nu_{asym}(CO_2Sn)$, 1365–1377m, $\nu_{sym}(CO)$; 523m (br), ν(Sn–O). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 6 H, J = 6.7, CH_3), 1.36–1.58 [m, 8 H, $CH_3(CH_2)_2$], 2.88 (q, 4 H, J = 15.3, CH_2) and 4.10 (t, 4 H, J = 6.7 Hz, OCH_2). ^{13}C NMR: δ 13.1 (CH_3), 19.0 (CH_2), 30.5 (CH_2), 43.6 (CH_2CO_2), 65.5 (OCH_2), 7.57 (tertiary C), 173.0 ($CH_2CO_2Bu^n$) and 180.6 (R_2CO_2Sn).

Hydrated bis(tetramethylammonium) bis(citrato)stannate(IV), $[NMe_4]_2[Sn\{C(O)(CO_2)(CH_2CO_2)(CH_2CO_2H)\}_2]\cdot 3.5H_2O$ 10. A dilute aqueous solution of tetramethylammonium tin(II) citrate-methanol(1/2) **5** was allowed to stand in an open conical flask. After several weeks the clear solution had evaporated to a colourless, viscous oil from which a crop of crystals formed on prolonged standing. These crystals could not be separated from the supernatant oil by filtration. A small number of crystals were removed by hand and carefully washed with a little ether [Found (Calc. for $C_{20}H_{41}N_2O_{17.5}Sn$): C, 33.8 (33.9); H, 6.02 (5.85); N, 4.0 (4.0)%]. Selected infrared data (cm^{-1}): 1727m (sh), $\nu_{asym}(CO_2H)$; 1644s (br), $\nu_{asym}(CO_2Sn)$. ^{1}H NMR (CD_3OD): δ 2.80 (m, 4 H, CH_2) and 3.19 [s, 12 H, $N(CH_3)_4$]. ^{13}C NMR: δ 56.5 [$N(CH_3)_4$], 47.1, 48.8 (CH_2), 76.4 (tertiary C), 176.0 (CH_2CO_2H), 178.2 (CH_2CO_2Sn) and 183.8 (R_2CO_2Sn).

Tin(II) laurate, $Sn[O_2C(CH_2)_{10}Me]_2$ 11. The compound $Sn(OMe)_2$ (1.0 g, 5.53 mmol) was suspended in freshly distilled tetrahydrofuran (thf) (50 cm^3) under an atmosphere of dinitrogen. A solution of lauric acid (2.21 g, 11.06 mmol) also in thf (20 cm^3) was added dropwise and the mixture refluxed for 30 min to yield a colourless solution. The solvent was evaporated *in vacuo* to afford the required compound in quantitative yield and analytically pure form [Found (Calc. for $C_{24}H_{46}O_4Sn$): C, 55.7 (55.5); H, 8.90 (9.21)%]. ^{1}H NMR (C_6D_6): δ 0.91 (s, 6 H, CH_3), 1.28 [s, 32 H, $(CH_2)_8$], 1.64 (s, 4 H, CH_2CH_3) and 2.27 (s, 4 H, CH_2CO_2). ^{13}C NMR: δ 14.2 (CH_3), 23.1, 25.6, 29.6, 29.7, 30.0, 30.1, 32.3, 36.4 (CH_2) and 182.2 (CO_2Sn).

Also prepared by the same method were: tin(II) palmitate, $Sn[O_2C(CH_2)_{14}Me]_2$ **12** [Found (Calc. for $C_{32}H_{62}O_4Sn$): C, 61.1 (61.0); H, 9.86 (10.20)%]; ^{1}H NMR (C_6D_6) δ 0.91 (s, 6 H, CH_3), 1.32 [s, 48 H, $(CH_2)_{12}$], 1.65 (s, 4 H, CH_2CH_3) and 2.27 (s, 4 H, CH_2CO_2); ^{13}C NMR: δ 14.2 (CH_3), 23.0, 25.6, 29.6, 29.7, 29.9, 30.1, 32.3, 36.3 (CH_2) and 182.0 (Co_2Sn); tin(II) sterate, $Sn[O_2C(CH_2)_{16}Me]_2$ **13** [Found (Calc. for $C_{36}H_{70}O_4Sn$): C, 63.1 (63.0); H, 10.22 (10.50)%]; ^{1}H NMR (C_6D_6): δ 0.90 (s, 6 H, CH_3), 1.34 [s, 56 H, $(CH_2)_{14}$], 1.63 (s, 4 H, CH_2CH_3) and 2.25 (s, 4 H, CH_2CO_2); ^{13}C NMR: δ 14.2 (CH_3), 22.9, 25.5, 29.6, 29.7, 29.9, 30.1, 32.3, 35.9 (CH_2) and 182.1 (CO_2Sn).

X-Ray crystallography

Compound 7. A crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm was mounted in a Lindemann capillary with some methanol and used for data collection.

Crystal data. $C_9H_{14}O_8Sn$, M = 368.9, monoclinic, space group $P2_1/c$, a = 9.793(6), b = 10.416(5), c = 12.849(6) Å, β = 104.21(4)°, U = 1270.6 $Å^3$, Z = 4, D_c = 1.92 g cm^{-3}, μ(Mo-Kα) = 20.4 cm^{-1}, F(000) = 728.

Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2 \leqslant \theta \leqslant 22°$. 1776 Reflections were collected of which 1261 were unique with $I \geqslant 3\sigma(I)$. Data were corrected for Lorentz-polarization effects and also for absorption [32] (maximum and minimum absorption corrections 1.148 and 0.850). The structure was solved by Patterson methods and refined using the SHELX [33,34] suite of programs. In the final least-squares cycles all atoms were refined anisotropically. Hydrogen atoms were included at calculated positions (C–H 0.96 Å) where relevant, except in the case of the methanolic proton [H(8)] which was located in the penultimate Fourier-difference map and refined. All hydrogen atoms were given a common isotropic thermal parameter (0.093 $Å^2$). Final residuals after 10 cycles of least squares were R = 0.0245, R' = 0.0269, for a weighting scheme of $w = 3.8581/[\sigma^2(F) + 0.000\,270(F)^2]$. Maximum final shift/e.s.d. was less than 0.0005. The maximum and minimum residual electron densities were 0.32 and −0.34 e $Å^{-3}$, respectively, in the region of the tin atom and as such have no chemical significance.

Compound 10. A crystal of approximate dimensions 0.5 × 0.5 × 0.2 mm was used for data collection.

Crystal data. $C_{40}H_{82}N_4O_{35}Sn_2$, M = 706.2, triclinic, space group $P\bar{1}$ (no. 2), a = 12.610(2), b = 15.571(5), c = 15.967(9) Å, α = 83.24(19), β = 76.70(5), γ = 75.91(4)°, U = 2952.9 $Å^3$, Z = 4, D_c = 1.59 g cm^{-3}, μ(Mo-Kα) = 9.4 cm^{-1}, F(000) = 1460.

Data were measured on the FAST system at the EPSRC X-ray crystallographic service (University of Wales, Cardiff). 119 88 Reflections were collected over the accessible reciprocal sphere of which 4536 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz-polarisation but not for absorption. The structure was solved and refined as above. In the final least-squares cycles the tin atoms were refined anisotropically. All other atoms were treated isotropically. Refinement was conducted in three blocks: one block for each of the cations, the anions and the water molecules, respectively. Hydrogen atoms were not included. Of the oxygen atoms, O(5′) and O(8′) were included at half occupancies. Final residuals after 44 cycles of blocked-matrix least squares were $R = R'$ = 0.0513. The maximum and minimum residual electron densities were 0.43 and −0.62 e $Å^{-3}$.

Despite a reasonably acceptable R factor, this structure did not converge well. Attempted anisotropic refinement resulted in unsatisfactory thermal parameters for many atoms. Similarly, efforts to apply a weighting scheme either before or after an empirical absorption correction proved fruitless and shift/e.s.d. values remained high throughout refinement. Sample quality may account for some of the above but the very large error of 0.19° in α may also have introduced some systematic error into the data set.

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