A novel macrocyclic dimeric dicarboxylato distannoxane assembled from a flexible dicarboxylic acid

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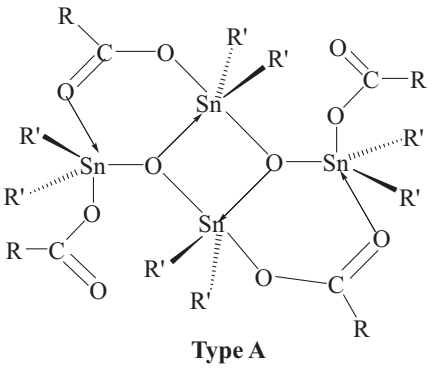
The novel macrocyclic complex $[(Bu_2Sn)_2OL]_2{\bullet}CH_3CN$ **(2)** has been prepared from the flexible dicarboxylic acid, LH_2, (**1**). Single crystal X-ray diffraction shows that complex **2** has a centrosymmetric structure, with a central rhomboid cyclic $Bu_4Sn_2O_2$ unit, linked at the oxygen atoms to two exocyclic tin atoms. The dicarboxylate ligands bridge exocylic and endocyclic tin atoms, completing two rings each of 22 atoms, and two of the four carbonyl oxygen atoms coordinate to the exocyclic tin atoms, to raise their coordination state to five and complete two more six-membered, rings.

Keywords: tin complex, organotin(IV) compounds, crystal structures, dicarboxylic acid ligands

In the past several decades, organotin carboxylates have emerged as an important class of compounds and attracted much research attention owing to their significant anti-tumour activity and catalytic activity and also their considerable structural diversity.[1-5] Depending on the carboxylic acid used and the stoichiometry of the reactants, various organotin carboxylates such as monomers, dimers, tetramers, oligomeric ladders and hexameric drums can be produced. Among these organotin carboxylates, the dicarboxylato tetraorganodistannoxanes with the general formula $\{[R'_2Sn(O_2CR)]_2O\}_2$ adopt five types of crystal structures in the crystalline state.[6,7] All these structural forms involve a centrosymmetric structure built up around a planar, four-membered cyclic Sn_2O_2 unit with two exocyclic Sn atoms which are five-coordinate. Each of the two exocyclic five-coordinate Sn atoms is bound to one bridging O atom of the four-membered ring, making these O atoms tri-coordinate. However, the small differences or the combination of very subtle factors based on the ligating mode between carboxylate groups and Sn atoms lead to the preference for a particular carboxylate to adopt a particular type of structure. For the structure type A as shown in Fig. 1, by far the predominant structure form, the two independent carboxylate groups are characterised by two distinct ligating modes.[8-10] One is unidentate and coordinated exclusively to the exocyclic Sn atoms. The other is bidentate with one O atom of the carboxylate group being coordinated to the exocyclic Sn atom and the other O atom to the endocyclic Sn atom. For type B, it retains the same Sn_2O_2 unit as existing in Type A structures, but the two bidentate bridging carboxylates each utilise only one O atom in bridging the two Sn centres.[11-13] As a result, the type B has a central core consisting of a ladder structure of three condensed four-membered rings.

Keeping in view the structural and biological diversity of organotin carboxylates and in connection with our interest in the coordination chemistry of organotin compounds with different carboxylic acids, we now present the preparation and characterisation of a novel complex $[(Bu_2Sn)_2OL]_2{\bullet}CH_3CN$ (**2**), where LH_2 is a symmetric and flexible dicarboxylic acid (**1**). Single crystal X-ray diffraction studies reveal that complex **2** adopts a Type A structure in the crystalline state, with the Sn_2O_2 unit of the centro-symmetric dimer connected to two quite different macroheterocycles.

The ligand **1** and the complex **2** were characterised by means of FTIR and NMR spectra. In the IR spectrum of **1**, the strong bands at 3440 and 2860 cm^{-1} were assigned to the O–H stretching motion and the ν(OH···O) mode due to the intra- and inter- molecular H-bonding. Moreover, the ν_{as}(COO) and ν_{sym}(COO) bands at ν1735 and 1674 cm^{-1} for **1** disappeared, while two types of COO absorption bands were observed at 1692, 1514 cm^{-1}[ν_{as}(COO)] and at 1454, 1334 cm^{-1}[ν_{sym}(COO)] for the complex **2**, respectively. The disappearance or shifts of these absorptions in the spectrum of complex **2** indicate that there is interaction between a carboxylate group and the metal ions in two distinct ligating modes. The difference Δ [ν_{as}(COO)–ν_{sym}(COO)] between these frequencies for **2** is close to that found for a unidentate chelate mode (*ca* 238 cm^{-1}) and a bridging bidentate carboxylato group (*ca* 180 cm^{-1}), respectively.[9] Two bands at 435 and 423 cm^{-1} for **2** are assigned to symmetric and asymmetric $(SnO)_2$ vibrations, indicating nonlinear O–Sn–O moieties. The absorption bands at 543 cm^{-1} are attributed to ν(Sn-C) stretching modes.[14,15]



Type A

Fig. 1 Type A dimeric organotin carboxylate, $\{[R'_2Sn(O_2CR)]_2O\}_2$.

A view of the distannoxane unit in complex **2** is shown in Fig. 2. The ORTEP drawing of complex **2** is shown in Fig. 3. Each cell in the crystal has one molecule of the complex **2** and one molecule of acetonitrile. The selected bond lengths and angles are listed in Table 1.

The structure of complex **2** is centro-symmetric and features a central rhomboid cyclic $Bu_4Sn_2O_2$ unit with two exocyclic five-coordinate Sn atoms linked at the O atoms of the four-membered ring. The central rhomboid cyclic $Bu_4Sn_2O_2$ unit is present in the dimeric tetraorganodistannoxanes of planar ladder arrangement with distorted square-bipyramidal geometry around the four five-coordinated tin centres, Sn(1), Sn(1A), Sn(2) and Sn(2A). In the molecule, the two O atoms of the $Bu_4Sn_2O_2$ unit are tridentate, of which the O(9) atom links three Sn(1), Sn(1A) and Sn(2) atoms and O(9A) links three Sn(1), Sn(1A) and Sn(2A) atoms. The bond distances

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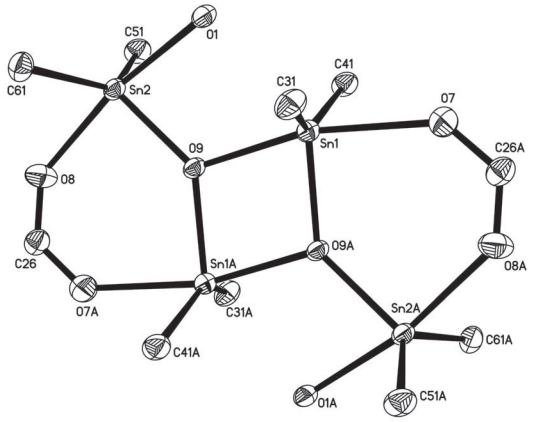


Fig. 2 View of the distannoxane unit in complex **2**.

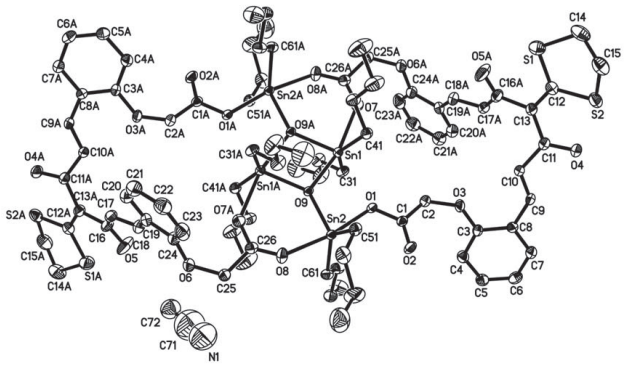


Fig. 3 ORTEP drawing of complex $[(Bu_2Sn)_2OL]_2 \cdot CH_3CN$ (**2**).

of Sn(1)–O(9), Sn(1)–O(9A) and Sn(2)–O(9) are 2.146(4) Å, 2.055(3) Å and 2.028(3) Å, respectively, which are close to Sn–O distances found in the type A compounds.[7-10] The Sn(1), O(9), Sn(1A), O(9A) atoms form one exocyclic six-membered chelating ring and the Sn(1), O(7), C(26A), O(8A), Sn(2A), O(9A) and Sn(1A), O(7A), C(26), O(8), Sn(2), O(9) form two endocyclic six-membered chelating rings, respectively. Additional links between the endo- and exo-cyclic Sn atoms are provided by bidentate carboxylate ligands that form essentially symmetrical bridges (Sn(1)–O(7) 2.282(5) Å and Sn(2)–O(8) 2.228(5) Å). Each exocyclic Sn atom is coordinated by a monodentate carboxylate ligand (Sn(2)–O(1) 2.190(4) Å). This configuration leads to five coordination Sn centres, each existing in a distorted trigonal bipyramidal geometry. The trigonal plane about Sn(1) is defined by C(31), C(41) and O(9A) atoms with the axial positions being occupied by the O(7) and O(9) atoms [O(7)–Sn(1)–O(9) 165.90(14)°], and the Sn(1) atom lies 0.1936 Å out of this plane in the direction of the O(9) atom. For the Sn(2) atom, the trigonal plane is defined by C(51), C(61) and O(9) atoms and the axial positions occupied by the O(1) and O(8) atoms [O(1)–n(2)–O(8) 169.50(15)°], and the Sn(2) atom lies 0.0029 Å out of this plane in the direction of the O(1) atom.

The endocyclic tin atom Sn(1) forms five primary bonds: one to the carboxylate oxygen atom O(7), two to the O(9) and O(9A), and two to the tin-bound *n*-butyl groups. In addition, the Sn(1) makes a close contact of 2.634 Å with the O(1) atom. The contact is significantly less than 3.68 Å, the sum of the van der Waals radii for Sn and O atoms).[17] It is observed that the bond angle C(31)–Sn(1)–Sn(41) is 143.2(2)°, which is 8.8° wider than that of C(51)–Sn(2)–C(61). This phenomenon is attributed to the weak coordination of O(1) and Sn(1).

It is of interest that the two carboxylate groups of dicarboxylic acid **1** both participate in the coordination to the Sn atoms but in distinct ligating modes, namely one is monodentate and coordinated exclusively to the exocyclic Sn atoms, whereas the other is bidentate linked with a pair of exo- and endo-cyclic Sn atoms. As a result, complex **2** exhibits a novel macrocyclic structure with a central rhomboid cyclic $Bu_4Sn_2O_2$ unit joining two macroheterocycles.

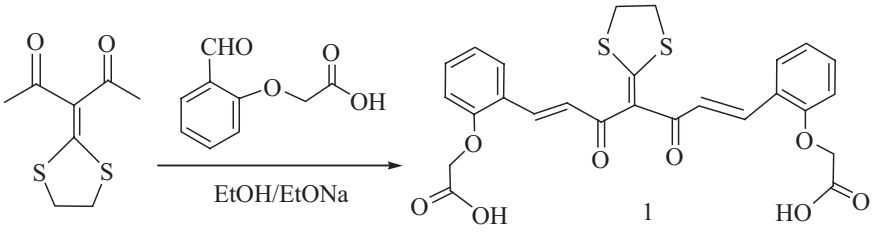
Experimental

Elemental analyses were carried out on a Perkin-Elmer PE 2400 CHN instrument and by gravimetric analysis for Sn. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 MHz spectrometer. IR spectra (KBr pellets) were recorded on an Alpha Centauri FI/IR spectrometer (400-4000 cm^{-1} range).

2-(2-Formylphenoxy)acetic acid was obtained from commercial sources and used without further purification. 3-(1,3-dithiolan-2-ylidene)pentane-2,4-dione was prepared by a modified literature method.[18] Solvents were used without purification.

Synthesis of ligand **1**: To a solution of 2-(2-formylphenoxy)acetic acid (3.60 g, 20 mmol) and 3-(1,3-dithiolan-2-ylidene)pentane-2,4-dione (2.02 g, 10 mmol) in 150 ml ethanol, sodium ethoxide (44 mmol, 1.0 g sodium dissolved in 20 ml ethanol) was added dropwise at 0°C within 30 minutes. The reaction mixture was stirred for 10 h at room temperature, then poured into cold water (*ca* 100 ml). After neutralisation with aqueous HCl (20%), a yellow solid was precipitated, which was collected by filtration and washed with water. The pure product was obtained by recrystallisation from ethanol as a yellow powder, yield 65%, m.p. 170–172°C. Anal. Found (Calc) for $C_{26}H_{22}O_8S_2$: C, 59.33(59.30), H, 4.25(4.21)%. IR: 3440 cm^{-1}, 1735 cm^{-1}, 1674 cm^{-1}, 1626 cm^{-1}, 1480 cm^{-1}, 1377 cm^{-1}, 1220 cm^{-1}. ^{1}H NMR (DMSO-d_6, δ): 3.65(s, 4H), 4.66 (s, 4H), 7.03 (d, 2H, J = 16.0 Hz), 7.49(d, 2H, J = 16.0 Hz), 6.80–6.78,7.14–7.23 (m, 8H), 11.25(s, 2H). ^{13}C NMR (DMSO-d_6, δ): 37.88, 66.02, 112.10, 113.81, 123.27, 125.39, 128.30, 128.75, 143.51, 149.84, 150.46, 170.74, 175.45, 187.98.

Synthesis of complex **2**: The mixture of di-*n*-butyltin oxide (1.24 g, 5.0 mmol) and LH_2(**1**) (2.63 g, 5.0 mmol) in 80 ml benzene was refluxed for 10 h and the binary azeotrope water/benzene was distilled off with a Dean–Stark condenser. The resulting clear solution was reduced to a small volume under reduced pressure. Drops of acetonitrile were added and after slow evaporation, yellow crystals were grown. The product was collected by filtration, washed with acetonitrile and dried *in vacuo*, yield 61%, m.p. 176–178°C. Anal. Found (Calc) for $C_{84}H_{112}O_{18}S_4Sn_4 \cdot 0.5CH_3CN$: C, 50.1 (50.03), H, 5.55 (5.61), Sn, 23.3 (23.27), N, 0.71 (0.67)%. IR: 1692, 1624, 1514, 1454, 1334, 1223, 561, 543, 435, 423 cm^{-1}. ^{1}H NMR (DMSO-d_6, δ): 0.83 (t, 24H), 1.25–1.57 (m, 48H), 3.38 (s, 8H), 4.67 (s, 8H), 6.72 (d, 4H, J = 15.6 Hz), 6.90 (d, 4H, J = 15.6 Hz,), 7.22–7.99 (m, 16H). ^{13}C NMR (DMSO-d_6, δ): 13.53, 26.13, 26.45, 26.74 (4 × C), 37.14, 65.00, 111.52, 121.48, 124.46, 127.93, 128.31, 130.06, 131.074, 138.40, 156.78, 177.33, 188.77.



Scheme 1 The preparation of dicarboxylic acid **1**.

Table 1 Selected bond distance (Å) and angles (°) of complex **2**

Sn(1)–O(9A)	2.055(3)	Sn(2)–O(9)	2.028(3)
Sn(1)–C(31)	2.110(6)	Sn(2)–C(61)	2.106(6)
Sn(1)–C(41)	2.119(5)	Sn(2)–C(51)	2.124(6)
Sn(1)–O(9)	2.146(4)	Sn(2)–O(1)	2.190(4)
Sn(1)–O(7)	2.282(5)	Sn(2)–O(8)	2.228(5)
O(9)–Sn(1A)	2.054(4)		
O(9A)–Sn(1)–C(31)	107.48(19)	O(9)–Sn(2)–C(61)	113.68(19)
O(9A)–Sn(1)–C(41)	106.50(19)	O(9)–Sn(2)–C(51)	111.9(2)
C(31)–Sn(1)–C(41)	143.2(2)	C(61)–Sn(2)–C(51)	134.4(2)
O(9A)–Sn(1)–O(9)	75.68(14)	O(9)–Sn(2)–O(1)	76.84(14)
C(31)–Sn(1)–O(9)	101.4(2)	C(61)–Sn(2)–O(1)	96.3(2)
C(41)–Sn(1)–O(9)	100.3(2)	C(51)–Sn(2)–O(1)	94.0(2)
O(9A)–Sn(1)–O(7)	90.39(15)	O(9)–Sn(2)–O(8)	92.81(16)
C(31)–Sn(1)–O(7)	84.6(2)	C(61)–Sn(2)–O(8)	86.2(2)
C(41)–Sn(1)–O(7)	81.4(2)	C(51)–Sn(2)–O(8)	91.4(2)
O(9)–Sn(1)–O(7)	165.90(14)	O(1)–Sn(2)–O(8)	169.50(15)
C(26A)–O(7)–Sn(1)	135.5(5)	Sn(2)–O(9)–Sn(1)	120.06(16)
C(26)–O(8)–Sn(2)	135.8(5)	Sn(1A)–O(9)–Sn(1)	104.32(14)
Sn(2)–O(9)–Sn(1A)	135.17(19)		

Crystal data (**2**): $C_{86}H_{115}NO_{18}S_4Sn_4$, *Mr* = 2053.79, monoclinic, *P2/n*, *a* = 17.030(3) (2) Å, *b* = 11.915(2) Å, *c* = 23.470(5) Å, β = 102.40(3)°, *V* = 4651.4(16) (4) Å^3, *Z* = 2, *F*(000) = 2092, *D*x = 1.466 g cm^{-3}, μ = 1.214 mm^{-1}, T = 293(2) K, R_1 = 0.0515, wR_2 = 0.0874. Single-crystal X-ray diffraction data for **2** were recorded on a Bruker CCD Area Detector diffractometer by using the ω/φ scan technique with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Absorption corrections were applied by using multiscan techniques[18]. The structure was solved by direct methods with SHELXS-97[19] and refined by full-matrix least squares with SHELXL-97[20] within WINGX[21]. All nonhydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were refined as rigid groups.

CCDC 610953 contains the supplementary crystallographic data for (2). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

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References

1 Y. Arakawa, In *Chemistry of tin*, P.J. Smith (ed.) Blackie Academic and Professional, London, 1998, p. 388.
2 D. de Vos, R. Willem, M. Gielen, K.E. van Wingerden and K. Nooter, *Met. Based Drugs*, 1998, **5,** 179.
3 M. Gielen, P. Lelieveld, D. de Vos and R. Willem, In *Metal complexes in cancer chemotherapy*, B.K. Keppler (ed.) VCH, Weinheim, 1993, p. 369.
4 M. Gielen, *Coord. Chem. Rev*., 1996, **151,** 41.
5 M. Gielen, M. Biesemans, D. de Vos and R. Willem, *J. Inorg. Biochem*., 2000, **79,** 139.
6 E. R. T. Tiekink, *Appl. Organomet. Chem.*, 1991, **5,** 1.
7 V. Chandrasekhar, S. Nagendran and V. Baskar, *Coord. Chem. Rev.*, 2002, **235,** 1.
8 M. Kemmer, H. Dalil, M. Biesemans, J.C. Martins, B. Mahieu, E. Horn, D. de Vos, E.R.T. Tiekink, R. Willem and M. Gielen, *J. Organomet. Chem.*, 2000, **608**, 63.
9 D. Kovala-Demertzi, N. Kourkoumelis, A. Koutsodimou, A. Moukarika, E. Horn and E.R.T. Tiekink, *J. Organomet. Chem.*, 2001, **620,** 194.
10 M.I. Khan, M.K. Ballock and M. Ashfag, *J. Organomet. Chem.*, 2004, **689,** 3370.
11 E.R.T. Tiekink, M. Gielen, A. Bouhdid, M. Biesemans and R. Willem, *J. Organomet. Chem.*, 1995, **494,** 247.
12 V. Chandrasekhar, R.O. Day, J.M. Holmes and R.R. Holmes, *Inorg. Chem.*, 1988, **27,** 958.
13 N.W. Alcock and S.M. Roe, *J. Chem. Soc. Dalton Trans.*, 1989, 1589.
14 K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, 4th edn. Wiley, New York, 1980.
15 D. Kovala-Demertzi, V.N. Dokorou, J.P. Jasinski, A. Opolski, J. Wiecek, M. Zervou and M.A. Demertzis, *J. Organomet. Chem.*, 2005, **690,** 1800.
16 A. Bondi, *J. Phys. Chem.*, 1964, **68,** 441.
17 For reviews on the synthesis and application of α-oxo ketene (*S,S*)acetals, see (a) R.K. Dieter, *Tetrahedron*, 1986 **42,** 3029; (b) Y. Tominaga, *J. Heterocycl. Chem.,* 1989, **26,** 1167. For our work on α-oxo ketene (*S,S*)acetals, see (c) Q. Liu, G. Che, H. Yu, Y. Liu, J. Zhang, Q. Zhang and D. Dong, *J. Org. Chem.*, 2003, **68,** 9148; (d) X. Bi, D. Dong, Q. Liu, W. Pan, L. Zhao and B. Li, *J. Am. Chem. Soc.*, 2005, **127,** 4578; (e) D. Dong, X. Bi, Q. Liu and F. Cong, *Chem. Commun.*, 2005, **28,** 3580.
18 T. Higashi, *A program for absorption correction*, Rigaku Corporation, Tokyo, Japan, 1995.
19 G.M. Sheldrick, SHELXS-97, A *program for automatic solution of crystal structure*, University of Göttingen, Germany, 1997.
20 G.M. Sheldrick, SHELXL-97, *A program for crystal structure refinement*, University of Göttingen, Germany, 1997.
21 L.J. Farrugia, WINGX, *A Windows-based program for crystal structure analysis*, University of Glasgow, Glasgow, UK, 1988.