Dalton Transactions

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A novel macrocyclic organotin carboxylate containing a nona-nuclear long ladder†

Cite this: *Dalton Trans.*, 2013, **42**, 15387

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Received 27th February 2013,
Accepted 16th August 2013

DOI: 10.1039/c3dt50531f

www.rsc.org/dalton

A novel macrocyclic organotin(IV) carboxylate $\{[n\text{-Bu}_2\text{Sn(O)}]_9(\text{CH}_2\text{CH}_3)_2\text{L}\}\cdot 3\text{CH}_2\text{CH}_3\text{OH}$ (complex **1**) (L = (9-carboxymethyl-1,3,8,10-tetraoxo-3,8,9,10-tetrahydro-1*H*-anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinolin-2-yl)-acetic acid) was generated by the reaction of dibutyltin oxide with amide dicarboxylic acid L and characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy. X-ray crystallography diffraction analysis reveals that **1** is a centrosymmetric macrocycle and contains a nona-nuclear eight-fold-ladder-like organo-oxotin cluster. The preliminary luminescent properties of complex **1** have also been studied.

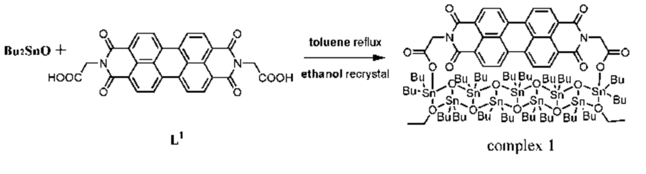
Introduction

The architectures of organotin macrocycles with large cavities and fascinating structures are attractive.[1] More and more attention has been paid to them for their potential applications in selective molecular recognition, storage, absorption, separation and catalysis.[2] Most of these compounds are prepared by appropriate reactions involving the corresponding organotins and carboxylic acids.[3] As we know, the structures of organotin carboxylate can be easily controlled by adjusting the type of carboxylic acid ligands, tin-R groups and metal-to-ligand molar ratio.[4] Ligands with multi-coordination and particular stereochemistry may lead different specific architectures.[5] To further the field of organotin carboxylate macrocycle and to explore novel esthetic architecture, we chose an amide dicarboxylic acid L as ligand. L is interesting for the following reasons: (a) strong coordination tendency with Sn and various bridging abilities inducing rich coordination modes; (b) long molecular lengths and long length between two carboxyl groups tending to build interesting macrocycle structures; (c) both rigid and flexible groups exist in it to form 2- and 3D moderately robust networks; (d) it possesses a big conjugated rigid planar structure which brings various properties. To our surprise, we obtained an unusual macrocyclic complex **1**. **1** is a mono-ligand 27-membered macrocycle carboxylate containing one nona-nuclear eight-fold-ladder-like organo-oxotin unit. A CSD search reveals that macrocyclic organotin complexes with a ladder structure are rarely studied. In addition to that, all of them are centrosymmetric ring with double ladders bridged by two ligands,[6] among which the longest four-fold ladder including seven tin atoms is from a double-ladder centrosymmetric macrocycle reported in literature.[6a] So **1** can be regarded as the organotin macrocycle with the longest ladder containing nine tin atoms, and the only single-ladder macrocycle organotin carboxylate bridged by one ligand at present. Moreover, few studies have been focused on the fluorimetric determination of organotin carboxylate, while **1** shows fluorescent properties revealed by the preliminary luminescent investigation.

Results and discussion

Synthesis

Through the reaction of Bu_2SnO with L refluxing in toluene, a red powder was obtained. After recrystallizing the products by ethanol, red crystals of complex **1** suitable for X-ray diffraction analysis were obtained (Scheme 1). Repeating the experimental procedures led the same result. Upon exposure to air, crystals of complex **1** became opaque within minutes, indicating a loss of solvent.[6b]



Scheme 1 Synthesis of complex **1**.

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† Electronic supplementary information (ESI) available: Synthesis of ligand L; selected bond lengths (Å) and angles (°) for complex 1. CCDC 923238. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50531f

Molecular structure

The molecular structure of complex **1** is shown in Fig. 1. Selected bond lengths and angles are listed in Table S1.† One macrocycle and three solvent ethanol molecules are included in the independent crystal cell. **1** is a 27-membered macrocycle composed of a nona-nuclear organo-oxotin skeleton [$Sn_9(\mu_3\text{-}O)_9$] and a ligand L chelated *via* monodentate coordination mode. Except O(1) and O(9) are bound by two Bu_2Sn units and a $-CH_2CH_3$ group, each bridging oxygen atom of the skeleton is coordinated with three Bu_2Sn units. Therefore all of them are three-coordinated and adopt planar trigonal geometry. All Sn atoms in **1** are five-coordinated, showing a trigonal bipyramid configuration but having two chemical environments. Sn(2)–Sn(8) are coordinated with three μ_3-O atoms and two C atoms from butyl groups, while for Sn(1) and Sn(9), one of the coordinated O atom [O(10) for Sn(1) and O(16) for Sn(9)] is from the carboxylate group of ligand L. The C–Sn–C angles are 131.9° and 148.7° for Sn(1) and Sn(9) respectively, much larger than those of Sn(2)–Sn(8) (117.1–120.9°), which are caused by the less space congestion of terminal position in the organo-oxotin unit. Axial O–Sn–O angles of Sn(1) and Sn(9) are 155.07 and 153.40° larger than those of Sn(2)–Sn(8) (148.50–151.35°) for the same reason. The $Sn_9(\mu_3\text{-}O)_9$ cluster demonstrates as a long ladder consist of eight twisted $Sn_2(\mu_3\text{-}O)_2$ distannoxane units. Excluding two end units, they are approximate to parallelogram proved by the Sn–O bond lengths of Sn(2)–Sn(8) ranging from 2.018 to 2.170 Å, and the related O–Sn–O (74.06–76.11°) and Sn–O–Sn (102.94–106.30°) angles listed in Table S1.† However, the both end units are more twisted with the Sn–O bond lengths of Sn(1) and Sn(9) owing larger span which range from 2.006 to 2.247 Å. And the relevant smaller O–Sn–O (71.34–73.11°) and larger Sn–O–Sn (100.32–113.9°) angles still indicate the torsion. All the related bond lengths and angles are similar to those found in the complexes of the category.[6] "Ladder" $Sn_9(\mu_3\text{-}O)_9$ are almost coplanar. For the plane surfaced by O(5), Sn(3) and Sn(7), the biggest deviations caused by O(1) and Sn(9) atoms are 0.101 and 0.104 Å respectively. Others are shorter among 0.001–0.094 Å. All the differences about Sn(1) and Sn(9) mentioned above are owing to their end ladder positions which lead smaller steric hindrance of the butyl groups on tin atoms. And for the steric hindrance, $Sn_9(\mu_3\text{-}O)_9$ ladder is not straight but zig-zag.

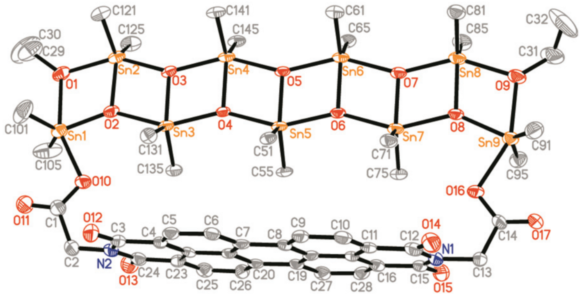

Fig. 1 The molecular structure of complex **1**. Part of the butyl groups are omitted for clarity.

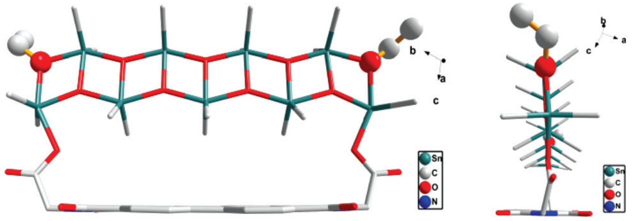

Fig. 2 The front and side views of **1**. Part of the butyl groups are omitted for clarity.

Ligand L chelates with the organo-oxotin ladder by monodentate coordination mode *via* Sn(1)–O(10) and Sn(9)–O(16) bonds with bond lengths 2.169 and 2.233 Å respectively. In addition to that, intramolecular distances Sn(1)···O(11) (2.935 Å) and Sn(9)···O(17) (2.981 Å) although longer than Sn–O covalent bond length are much shorter than the sum of the van der Waals radii of tin and oxygen (3.7 Å).[7a] They lie in the range of intramolecular Sn–O bond distances of 2.61–3.02 Å.[7b] Therefore the oxygen atoms O(11) and O(17) are involved in a weak coordinative interaction with tin.[7c,d] In consideration of this interaction, Sn(1) and Sn(9) could be described as hexa-coordinated and adopt a tetragonal bipyramidal geometry. The limber flexible "$-CH_2-$" groups of ligand L help to make the molecule cyclic annular. The ring is a 27-membered irregular macrocycle resembling almost a rectangle (Fig. 2) with the probable width 14.3 Å × 4.4 Å. And the plane of the "ladder" cluster is almost perpendicular to the big conjugated rigid plane of ligand L with the dihedral angle of 86.52° (see the side view of **1** in Fig. 2).

Besides the bonds mentioned above, intermolecular Sn(9)···O(17) interaction still exits with Sn···O distance 2.989 Å (Fig. 3). Sn(9) is the terminal atom of the "ladder" unit and O(17) is the carboxylate oxygen. This type of interaction helps complex **1** to form an intermolecular irregular ring A. A is eight-membered with the probable width 4.2 Å × 2.9 Å. In the spatial architecture of **1**, large aromatic conjugation systems of ligands from two different molecules are adjacent and face-to-face. The planes of them are paralleled with distance 3.350 Å and π···π interaction exists.[1f] With additional help of the π···π interactions, Sn(9)···O(17) interactions link complex **1** into a 1D infinite zig-zag chain along the *b* axis.

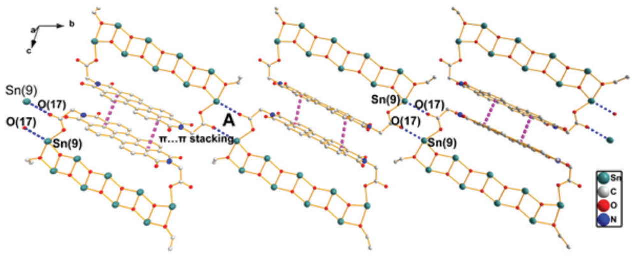

Fig. 3 1D chain structure of **1**. The butyl groups are omitted for clarity.

IR and NMR spectra

In the IR spectrum of **1** (Fig. S1†), the disappearance of a broad band in the region 3400–2800 cm^{-1} owing to COOH groups as the (O–H) stretching vibrations of ligand L indicates the replacement of the carboxylic acid proton by an alkyltin moiety in the complex formation.[2d,f] The $\Delta\nu$ (ν_{asym}COO–ν_{sym}-COO) value for complex **1** is 250 cm^{-1} larger than 200 cm^{-1}, standing for the unidentate chelate coordination mode of the carboxylate group,[2b,d,3a,4a] which is consistent with the X-ray structure. The absorption band at 598 cm^{-1} is assigned to the stretching frequency associated with Sn–O–Sn bond, indicating a Sn–O–Sn bridged structure, and the one at 541 cm^{-1} is attributed to the Sn–C bonds of the Bu$_2$Sn units. A strong band at 460 cm^{-1} is assigned to ν(Sn–O), indicative of a Sn–O coordinated structure.[2f,4b]

In the ^{1}H NMR spectrum of complex **1** (Fig. S2†), the signal for the COOH proton (11.94 ppm) of the free ligand L is absent due to the formation of the carboxylate.[2f] The spectrum shows expected integration and peak multiplicities for the hydrogen protons on the aromatic rings of ligand L in **1**. They appear almost in the same positions as in L at 7.95 and 7.13 ppm. The chemical shift for "–CH$_2$–" group of L in **1** is at 4.51 as single peak.[7d] Signals for the hydrogen protons on coordinated ethanol and butyl groups of tin can also be attributed appropriately.

Compared with the ^{13}C NMR spectrum of the free ligand L, a significant downfield shift of carbon resonances in the spectrum of **1** (Fig. S3†) is observed. The shift is thought to be a consequence of the electron density transfer from the ligand to the acceptor tin atoms.[4b,d] Single resonances at 168.45 and 166.20 ppm of **1** are assigned to COO and C=O groups respectively. Chemical shift for "–CH$_2$–" of L in **1** is at 48.74 ppm.[7d] The peaks of the aromatic rings, coordinated ethanol and butyl groups can be appropriately attributed. With the $^1J^{119}{}_{Sn-^{13}C}$ value being 527 Hz and by the use of the Holecek and Lycka equation,[8a] C–Sn–C value of 123° was calculated, which corresponds to the geometry of Sn atoms in **1**. These data are all consistent with the structure of **1**.

The ^{119}Sn NMR spectrum shows two resonances of equal intensity at −178.2 and −189.5 due to endocyclic and exocyclic tin atoms respectively. They are within the range corresponding to a typical five-coordinated species (−90 to −190),[8b] which is in accordance with the structure of **1** in the solid state.

UV-Visible and fluorescence spectra

The UV-Vis absorption spectrum of **1** in the solid state (Fig. S4†) was surveyed in 200–800 nm. It shows an intense absorption band at 228 nm and a moderate one at 358 nm in the relatively high-energy region, which are assigned to the ligand-centered $\pi \rightarrow \pi^*$ transition, and two strong bands in the low energy region (493 and 530 nm) corresponding to the LMCT- (ligand-to-metal charge transfer) and intraligand transitions of the perylene unit.[8c]

Coordination polymers with d^{10} metal center and organic ligand are promising candidates for photoactive materials with potential applications.[8d] The luminescent properties of complex **1** and free ligand L in the solid state have been investigated at room temperature with a 150 W xenon lamp as the excitation source. The fluorescence excitation spectrum of **1** (Fig. S5†) agrees with the UV-Vis absorption spectrum. The fluorescence emission spectra of **1** and ligand are given in Fig. S6.† The emission peak of the free ligand L is observed at about 679 nm with the excitation peak at 266 nm, which is generally caused by $S_1 \rightarrow S_0$ transition and probably attributable to the $\pi^* \rightarrow \pi$ transitions. On complexation of the ligand with the Sn(IV) atom, complex **1** was blue-shifted up to 641 nm (λ_{ex} = 380 nm). The blue-shift may be attributed to the coordination effects of the ligand L to Sn(IV), which increases the ligand conformational rigidity and reduces the nonradiative decay of LMCT.[8d]

Conclusion

In summary, we have synthesized and characterized a novel macrocyclic organotin carboxylate containing one nonanuclear eight-fold-ladder organo-oxotin unit. It is the longest "ladder" reported in the literature by far and the only single-ladder macrocycle organotin carboxylate at present. The aesthetic molecular structure of **1** supplements the group of organotin carboxylate. In addition, **1** shows fluorescent properties.

Experimental section

Materials and measurements

Di-*n*-butyltin oxide is commercial available and was used without further purification. L was prepared by a modified literature method.[8e] The solvents were purified according to standard procedures before use. The melting point was obtained with a Kofler micro-melting point apparatus and was uncorrected. Elemental analysis (C, H, N) was carried out on a Perkin-Elmer PE 2400 CHN instrument. IR spectrum (KBr pellets) was recorded on an Alpha Centauri FI/IR spectrometer (400–4000 cm^{-1} range). ^{1}H, ^{13}C NMR spectra were recorded on a Varian Mercury spectrometer operating at 300 and 75 MHz, respectively. The UV-Vis absorption spectrum was recorded by a Varian Cary 500i UV-Vis-NIR spectrophotometer. The luminescent properties of the ligand and complex were measured on a Perkin-Elmer FLS-920 spectrometer.

X-ray crystallography

Diffraction intensities for complex **1** were collected on a Bruker CCD Area Detector image plate diffractometer by using the ω/φ scan technique with Mo-Kα radiation (λ = 0.71073 Å). Absorption corrections were applied by using multiscan techniques. The structure was solved by direct methods with SHELXS-97[8f] and refined using SHELXL-97.[8g] All non-hydrogen atoms were refined with anisotropic temperature parameters; hydrogen atoms were refined as rigid groups. Crystal data for **1**: $C_{218}H_{394}N_4O_{39}Sn_{18}$, M = 5831.79, triclinic, space group

$P\bar{1}$, $Z = 1$, $a = 12.6937(7)$ Å, $b = 21.0320(12)$ Å, $c = 26.3364(14)$ Å, $\alpha = 107.0910(10)°$, $\beta = 99.2360(10)°$, $\gamma = 100.1300(10)°$, $V = 6445.4(6)$ Å^3, μ(Mo Kα) = 1.770 mm^{-1}, $F(000) = 2942$, GoF = 1.013, $D_c = 1.502$ g cm^{-3}. 41 016 reflections collected to give all the data for $R_1 = 0.1164$ and w$R_2 = 0.1667$, 24 951 of which were used in the refinement to give the final $R_1 = 0.0627$ and w$R_2 = 0.1374$ [$I > 2\sigma(I)$]. CCDC reference number 923238.

Synthesis of 1 {[*n*-Bu$_2$Sn(O)]$_9$(CH$_2$CH$_3$)$_2$L}·3CH$_2$CH$_3$OH

A solution of L (0.097 g, 0.1 mmol) and di-*n*-butyltin(IV) oxide (0.249 g, 1.0 mmol) in toluene (50 ml) was refluxed for 8 h using a Dean–Stark trap to facilitate the dynamic removal of the water formed in the reaction by azeotropic distillation. After cooling to room temperature, the solvent mixture was filtrated. The filtrate was allowed to slow evaporation of toluene at room temperature to afford a red powder. After recrystallized with ethanol, red crystals of complex **1** were obtained. Yield: 78.2%. Mp: >300 °C. Elemental analysis calcd for $C_{109}H_{197}N_2O_{20}Sn_9$: C, 44.77; H, 6.79; N, 0.96; Sn, 36.54%. Found: C, 44.81; H, 6.93; N, 0.95; Sn, 36.59%. IR (cm^{-1}): 1666 [s, ν(O═C)], 1611 [s, ν_{asym}(COO)], 1361 [s, ν_{sym}(COO)], 598 [m, ν(Sn–O–Sn)], 541 [m, ν(Sn–C)], 460 [s, ν(Sn–O)]. ^{1}H NMR (CDCl$_3$): δ 7.95 (d, 4H, J = 7.4 Hz, Ar–H), 7.13 (d, 4H, J = 7.4 Hz, Ar–H), 4.51 (s, 4H, –CH$_2$–), 3.34 (q, 4H, J = 6.7 Hz, –O–CH$_2$–), 1.15–1.60 (m, 114H, Sn–CH$_2$–CH$_2$–CH$_2$– and –O–C–CH$_3$), 0.90 (t, 54H, J = 7.2 Hz, Bu–H: –CH$_3$). ^{13}C NMR (dimethyl sulfoxide-*d*$_6$): δ 168.45 (2C, COO), 166.20 (4C, C═O), 132.82 (4C, Ar–C: C7, C8, C19, C20), 131.76 (4C, Ar–C: C4, C11, C16, C23), 130.32 (2C, Ar–C: C18, C21), 128.96 (8C, Ar–C: C5, C6, C9, C10, C25, C26, C27, C28), 126.51 (2C, Ar–C: C17, C22), 69.38 (2C, ethanol–C: –O–CH$_2$–), 48.74 (2C, –N–CH$_2$–), 28.35 (18C, Bu–C: –CH$_2$–), 26.12 (18C, Bu–C: –CH$_2$–), 16.26 (2C, ethanol–C: –CH$_3$), 13.64 (18C, Bu–C: –CH$_3$), 8.96 (18C, $^1J^{119}{}_{\mathrm{Sn-^{13}C}}$ = 527 Hz, Bu–C: Sn–CH$_2$–). ^{119}Sn NMR (dimethyl sulfoxide-*d*$_6$): −178.2, −189.5 ppm.

Acknowledgements

We acknowledged the Science and technology department of Jilin province (no. 20120440).

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