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ARTICLE

A Sulfonated Schiff Base Dimethyltin(IV) Coordination Polymer: Synthesis, Characterization and Application as a Catalyst for Ultrasound- or Microwave-Assisted Baeyer-Villiger Oxidation under Solvent-free Conditions†

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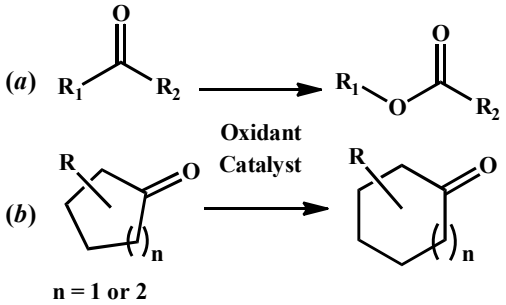
Abstract

Synthesis and crystal structure of the new dimethyltin(IV) compound $[SnMe_2(HL)(CH_3OH)]_n \cdot (0.5nCH_3OH)$ (**1**) derived from the Schiff base 2-[(2,3-dihydroxyphenyl)methylideneamino]benzenesulfonic acid (H_3L) are described. Despite having six potentially donating centres (one imine nitrogen, two phenoxo and three sulfonate oxygen atoms), the monoprotonated dianionic ligand (HL^{2-}) behaves as O,O,O-tridentate chelator. Single crystal X-ray diffraction revealed that **1** is a 1D coordination polymer with every tin(IV) ions bound to two methyl groups, a methanol molecule, two $O_{phenoxo}$ and one μ-$O_{sulfonate}$ atoms from HL^{2-}. The coordination polymer **1** was applied as heterogeneous catalyst for the Baeyer-Villiger oxidation of ketones to esters or lactones, using aqueous hydrogen peroxide as oxidant, under ultrasound (US) or microwave (MW) irradiation and solvent- and additive-free conditions. Overall conversions up to 76/82, 98/93, 93/89, 91/94, 83/90, 68/62 and 81/87% under US/MW irradiations were obtained with 3,3-dimethyl-2-butanone, cyclopentanone, 2-methylcyclopentanone, cyclohexanone, 3-methylcyclohexanone, benzophenone and acetophenone, respectively. The catalyst can be recycled up to five cycles without losing appreciable activity.

Introduction

There has been a tremendous development in the coordination chemistry of organotin compounds, enriched by the variety of their solid and solution structures and biological applications.[1,2] They are also used as heat stabilizers in industry[3] and as catalysts[4–9] for several important organic reactions and processes such as esterification,[4] production of urethane foams and elastomers,[5] polymerization[6] and epoxidation of olefins,[7] and curing of silicones.[8] Applications as oxidation catalysts for conversion of 1,2-diols into α-hydroxyketones are also known.[9] Finding new types of organotin compounds which could be useful for other oxidation catalyses with industrial significance is, therefore, a promising goal.

The Baeyer-Villiger (BV) oxidation is an important route (Scheme 1) to synthesize esters and lactones which are common synthetic intermediates with significance on the production of high valuable fine chemicals.[10]



Scheme 1 BV oxidation of (*a*) linear or (*b*) cyclic ketones to esters or lactones, respectively.

Usually, peroxyacids or peroxides have been used as the oxidant for this conversion[10,11] demonstrated for the first time by A. Baeyer and V. Villiger in the presence of peroxymonosulfuric acid.[12a–c] In recent years, several approaches to perform the BV oxidation according to sustainable chemistry principles have been proposed.[10d–f,12e–h,13] Among them are the use of milder and more atom-efficient oxidants, such as aqueous hydrogen peroxide, and of alternative energy sources such as microwave (MW) or ultrasound

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† Electronic Supplementary Information (ESI) available: Tables S1 and S2. Figs. S1–S7. CCDC 1483486 for **1** contains the supplementary crystallographic data for this paper. This CIF data can also be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. See DOI: 10.1039/x0xx00000x

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(US) irradiation.[13b,c] The use of a catalyst is required when milder oxidants are used. Tin(IV) centres, particularly in Sn-zeolite, have been experimentally and theoretically studied in this oxidation reaction.[10d,13a,d] Few other materials such as FAU-type stannosilicate,[13e] SnO_2 nanoparticle-decorated graphene oxide sheets,[13f] Fe_3O_4 magnetic nanoparticles,[13g] Fe_3O_4-l-dopa-Cu^{II}/Sn^{IV}@micro-mesoporous-SiO_2,[13h] InOx/TUD-1,[13i] and magnesium and/or calcium-containing natural minerals[13j] have also been used as catalysts for this reaction. We anticipate that a combination of substituted sulfonic acid (*e.g.*, sulfonated Schiff base),[14] an organotin(IV) centre and H_2O_2, could also be useful for this reaction. Thus, we targeted to synthesize a sulfonated Schiff base organotin compound with the aim to explore its catalytic activity towards the BV reaction.

On the other hand, sulfonic acid containing Schiff bases are rare and only a few copper[14] complexes are known. Some of them were applied in catalysis, mainly in alkane[14a,b] or alcohol oxidation[14c,h] and nitro-aldol (C–C coupling) reactions.[14d] Very recently, we have reported crystal structures and biological activities of the diorganotin(IV) complexes $[Sn(Et)_2(HL)(H_2O)]_2$ and $[Sn(n\text{-}Bu)_2(HL)(H_2O)]_2$ derived from the sulfonated Schiff base 2-[(2,3-dihydroxyphenyl)methylideneamino]benzenesulfonic acid (H_3L).[14g] Moreover, the successful catalytic applications of the sulfonated Schiff base copper complexes and the above mentioned importance of the Baeyer-Villiger oxidation inspired us to synthesize an organotin(IV) complex which could be useful for such a catalytic reaction under greener conditions, what constitutes the primary aim of the present study. Accordingly, the sulfonated Schiff base H_3L was reacted with $[SnMe_2Cl_2]$ in the presence of triethylamine (TEA) and herein we report the synthesis, crystal structure and catalytic activity towards the BV oxidation of the isolated dimethyltin(IV) based one dimensional coordination polymer $[SnMe_2(HL)(CH_3OH)]_n{\cdot}(0.5nCH_3OH)$ (**1**) (Scheme 2). To our knowledge, no sulfonated Schiff base organotin(IV) complex had been applied in the Baeyer-Villiger oxidation and this is the third sulfonated Schiff base organotin(IV) compound to be reported.

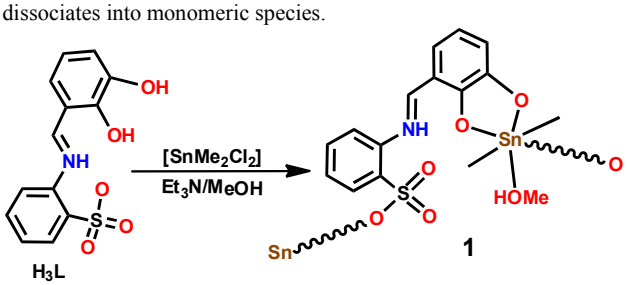
Results and discussion

Synthesis and characterization

The [1+1] condensation of 2,3-dihydroxybenzaldehyde and 2-aminobenzenesulfonic acid in aqueous methanol (1:2) leads to the formation of the Schiff base H_3L[14g] which, upon reaction with dimethyltin(IV) dichloride (used in the molar ratio of 1:1) in the presence of triethylamine (TEA, in a TEA:ligand molar ratio of 2:1) in methanol, produces the dimethyltin(IV) based 1D coordination polymer $[SnMe_2(HL)(CH_3OH)]_n{\cdot}(0.5nCH_3OH)$ (**1**) (Scheme 2) in a good yield (76%). A much lower yield (49%) was obtained with a higher amount of the base (TEA:ligand = 3:1). The metal complex was characterized by IR, NMR and ESI-MS spectroscopy (Figs. S1–S5, Electronic Supplementary Information), elemental and single crystal X-ray diffraction analyses.

In the IR spectrum (Fig. S1, ESI), it exhibits a medium intense absorption at 1639 cm^{-1} due to C=N vibration, comparable to that (1635 cm^{-1}) for the ligand. A pronounced shift of the C=N vibration was not observed as the imine nitrogen remains uncoordinated (see crystal structure description). The presence of the sulfonate group is evidenced by the medium intense band at 1384 cm^{-1} for **1**, which is comparable to that (1383 cm^{-1}) for the free H_3L.[14g]

The ^{119}Sn NMR (in DMSO-d_6) spectrum (Fig. S4, ESI) of **1** exhibits two signals at *ca.* –169 and –192 ppm, which could be possibly attributed to the presence of isomers in solution.[2i,14g,15] The observed ^{119}Sn NMR values suggest a penta-coordinated environment of the Sn atom[2f,14g,16] what is in agreement with the obtained ESI-MS (m/z, –ve mode, Fig. S5, ESI) spectra (in DMSO+MeOH solvent), indicating that the polymeric form of **1** dissociates into monomeric species.



Scheme 2 Synthesis of $[SnMe_2(HL)(CH_3OH)]_n{\cdot}(0.5nCH_3OH)$ (**1**).

Description of the crystal structure

The idealized ball and stick presentation of $[SnMe_2(HL)(CH_3OH)]_n{\cdot}(0.5nCH_3OH)$ (**1**) is depicted in Fig. 1 while the one dimensional polymeric network is presented in Fig. 2. Some selected bond length and angles are listed in Table 1. The single-crystal X-ray diffraction analysis reveals that compound **1** is the dimethyltin(IV) based coordination polymer, crystallizing in monoclinic *C*2/*c* space group.

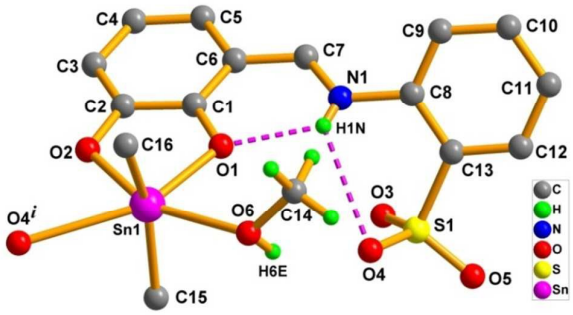


Fig. 1 Idealized ball and stick presentation of the crystal structure of **1**. Symmetry: *i*) 0.5–x, 0.5+y, 0.5–z.

The ligand HL^{2-} becomes highly distorted upon chelation to the tin(IV) ion, as indicated by the angle of 55.80º between the least square planes of the two phenyl rings, much larger than that (*ca.* 4º) found in the free pro-ligand,[14g] and also exceeds the values found in the ethyl or *n*-butyl analogue (44.63º or 41.26º).[14g] The basal SnO_4 metallic core formed by the two $O_{phenoxo}$ (O1 and O2), one $O_{methanol}$ (O6) and one (O4) of the $O_{sulfonate}$ atoms, is nearly coplanar with the attached phenyl ring. The two methyl ligands occupy the axial coordination sites and give rise to a C–Sn–C angle of 152.40(15)º. Equivalent vicinal units are interconnected by the sulfonate bridge to generate a one dimensional *zigzag* coordination polymeric chain (Fig. 2).

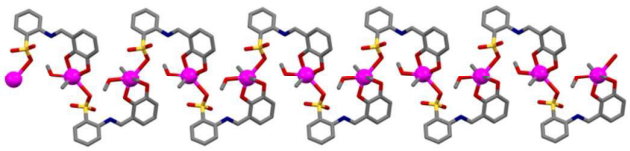


Fig. 2 One dimensional *zigzag* polymeric chain in **1**. Pink balls present tin atoms and H-atoms are omitted for clarity.

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The C_2O_4 metal coordination environment can be described as distorted trigonal prism, the trigons being defined by one $O_{phenoxo}$, one C_{methyl} and either the $O_{methanol}$ or the $O_{sulfonate}$ atoms (Fig. 3).

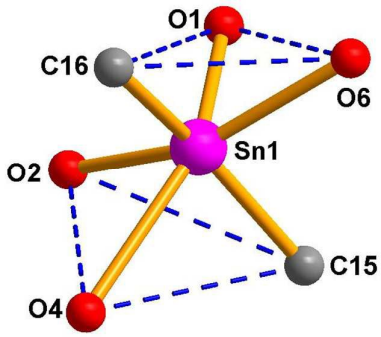


Fig. 3 The distorted trigonal prismatic molecular geometry at tin(IV) centre in the crystal structure of **1**.

The bond distances and angles (Table 1) are comparable to those previously reported for analogous diorganotin(IV) compounds derived from the same ligand.[14g]

Table 1 Selected bond distances (Å) and angles (º) in **1**

In the HL^{2-} moiety	
C=N	1.295(4)
C_{phenyl}–N_{imine}	1.429(4)
C_{phenyl}–$O_{phenoxo}$	1.332(4), 1.342(3)
∠ between the l.s. planes of the aromatic rings	55.80
Surrounding the Sn(IV) centre	
Sn···Sn(closest)	6.021
Sn–C_{methyl}	2.099(3), 2.103(3)
Sn–$O_{phenoxo}$	2.1221(19), 2.109(2)
Sn–$O_{methanol}$	2.351(2)
Sn–$O_{sulfonate}$	2.685
$O_{phenoxo}$–Sn–$O_{phenoxo}$	77.60(8)
$O_{phenoxo}$–Sn–$O_{sulfonate}$	151.61,74.01
$O_{methanol}$–Sn–$O_{sulfonate}$	131.11
C_{methyl}–Sn–C_{methyl}	152.40(15)

The crystal structure of **1** is stabilized by *intra*-chain N–H···O and O–H···O interactions. The amine group simultaneously donates to the $O_{phenoxo}$ (O1) and $O_{sulfonate}$ (O4) atoms, thus forming six-membered HNC_3O and HNC_2SO rings (Fig. 1), respectively, while the alcohol (O6) donates to the $O_{phenoxo}$ ($O2^{ii}$) atom (Table S1 and Fig. S6, ESI) of another unit of same chain. *Inter*-chain C–H···O weak contacts (Table S1) involving the C3 and C9 aromatic and C7 imine carbons as donors, and the sulfonate O3 and O5 atoms as acceptors, extends the structure to the third dimension (Fig. S7, ESI).

It is worthwhile to mention that there are several dimethyltin(IV) compounds[17–27] which contain different types of bridging moieties *e.g.*, carboxylate,[17] phosphonate,[18] hydroxo,[19] oxo,[20] sulfate,[21] azide,[22] selenite,[23] arsenate,[24] 4,4'-bipyridine[25] and sulfonate.[18c,d,19b,c,26] A few Schiff base dimethyltin(IV) complexes[28] are also known but a sulfonated Schiff base has never been utilized to synthesize dimethyltin(IV) compounds. We have synthesized a dimethyltin(IV) coordination polymer, which is the third diorganotin compound derived from a sulfonated Schiff base after the diethyl- and di-*n*-butyl ones.[14g] In addition, we have investigated its catalytic behaviour towards the Baeyer-Villiger oxidation (see below).

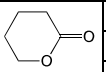
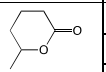
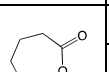
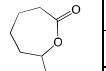
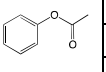
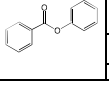
Baeyer-Villiger oxidation of ketones

As mentioned above, safety and environmental requirements have led to the replacement of peroxyacids (as oxidizing agents) by hydrogen peroxide, in the Baeyer-Villiger (BV) oxidation of ketones, what, however, needs the presence of a catalyst to activate the ketone and further drive the reaction.

The dimethyltin(IV) based coordination polymer $[SnMe_2(HL)(CH_3OH)]_n.(0.5nCH_3OH)$ (**1**) was tested for the BV oxidation of cyclic (cyclo-pentanone or -hexanone, 2-methylcyclopentanone and 3-methylcyclohexanone) and acyclic aromatic (acetophenone and benzophenone) or aliphatic (3,3-dimethyl-2-butanone) ketones to the respective lactones and esters, with hydrogen peroxide (30% aq. solution) as the oxidizing agent, under solvent-free conditions. The catalytic reactions were conducted at room temperature or at a mild temperature (60 ºC) under conventional (oil bath) heating (with magnetic stirring), microwave and sonochemical conditions. The effects of a variety of reaction parameters, such as reaction time, oxidant type and ratio, type of solvent, amount of catalyst or reaction temperature, on the activity of the catalyst were studied towards the optimization of the processes for all ketones and catalytic procedures (conventional heating, MW and US). The results are shown in the ESI, Table S2, and discussed below.

Compound **1** is highly active in the BV oxidation reaction. Ketone conversions are dependent on the substrates and on the procedure used (Table 2). For all substrates, microwave (MW) or ultrasound (US) irradiation dramatically reduced the oxidation time improving yields and purity of the desired lactones or esters. Table 2 compares the catalytic results obtained after 1 h reaction time for the different methods used.

Table 2 Baeyer-Villiger oxidation of several ketones catalyzed by **1** (selected data)[a]

Entry	Procedure	Temp. / ºC	Ketone	Product	Conv.[b] /%	Select.[c] / %	TON[d]
1	magnetic stirring	r.t.			4	42	17
2		60			6	51	31
3	ultrasound	r.t.			30	80	240
4		60			76	99	752
5	microwave	60			82	86	705
6	magnetic stirring	r.t.			10	67	67
7		60			39	54	221
8	ultrasound	r.t.			54	72	389
9		60			98	100	980
10	microwave	60			93	98	911
11	magnetic stirring	r.t.			13	55	72
12		60			22	67	147
13	ultrasound	r.t.			51	84	428
14		60			93	100	930
15	microwave	60			89	86	765
16	magnetic stirring	r.t.			9	71	64
17		60			37	53	196
18	ultrasound	r.t.			58	88	510
19		60			91	100	910
20	microwave	60			94	92	865
21	magnetic stirring	r.t.			11	67	73
22		60			43	55	237
23	ultrasound	r.t.			57	98	559
24		60			83	100	830
25	microwave	60			90	77	693
26	magnetic stirring	r.t.			7	72	50
27		60			23	67	154
28	ultrasound	r.t.			63	89	561
29		60			87	93	809
30	microwave	60			81	88	723
31	magnetic stirring	r.t.			3	89	27
32		60			12	86	103
33	ultrasound	r.t.			54	91	491
34		60			62	87	593
35	microwave	60			68	79	537

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[a] Reaction conditions (unless stated otherwise): **1** (2.0 μmol), 2.0 mmol of ketone, H_2O_2 (2.0 mmol), 60 min, r.t. or 60 ºC. Yield and TON determined by GC analysis. [b] Moles of converted (reacted) substrate per mole of substrate. [c] Moles of lactone (or ester) per mole of converted substrate. [d] Turnover number (moles of product per mol of **1**).

Complex **1** exhibits a remarkable selectivity (up to 100%) towards the catalytic formation of lactones or esters from cyclic or acyclic (aromatic or aliphatic) ketones, respectively (Table 2; see Fig. 4 for oxidation of 2-methylcyclohexanone) particularly when US radiation was used. Complete regioselectivity was observed for the BV oxidations of the tested unsymmetrical ketones, 2-methylcyclopentanone, 2-methylcyclohexanone, 3,3-dimethyl-2-butanone and acetophenone, to afford δ-hexalactone, 6-methylhexanolide, *tert*-butylacetate or phenylacetate, respectively (Table 2). In all cases, the formal insertion of the oxygen atom between the carbonyl and the more substituted Cα atom was the preferred route.

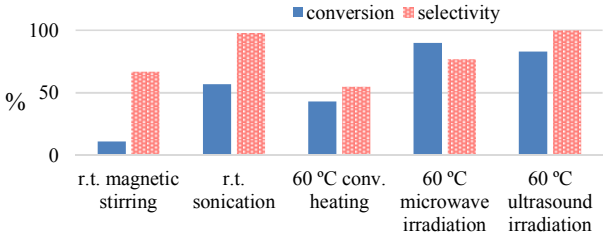


Fig. 4 Conversion of 2-methylcyclohexanone and selectivity for ε-caprolactone obtained upon BV oxidation catalyzed by **1** after 1 h under different reaction conditions.

Our MW- or US-assisted catalytic systems using **1** are much more selective and active than Sn(IV) salts such as $SnCl_4$ (compare entries 6–10 of Table 2 and Table 3). It was also reported that, in the presence of $SnCl_4$, 99% of cyclohexanone is converted after 24 h oxidation (with 30% aq. H_2O_2 in 1,2-dicloroethane) with a selectivity to ε-caprolactone of only 60%.[28]

Table 3 Baeyer-Villiger oxidation of cyclopentanone to γ–butyrolactone catalyzed by $SnCl_4$ (selected data)[a]

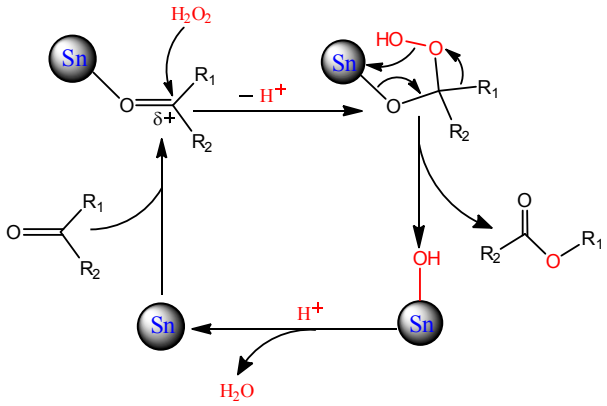
Entry	Procedure	Temp. / ºC	Conv. [b] /%	Select.[c]	TON[d]
1	magnetic stirring	r.t.	4	80	32
2		60	11	77	85
3	ultrasound	r.t.	32	62	198
4		60	63	48	302
5	microwave	60	71	57	405

[a] Reaction conditions (unless stated otherwise): $SnCl_4$ (2.0 μmol), 2.0 mmol of ketone, H_2O_2 (2.0 mmol), 60 min, r.t. or 60 ºC. Yield and TON determined by GC analysis. [b] Moles of converted (reacted) substrate per mole of substrate. [c] Moles of lactone per mole of converted substrate. [d] Turnover number (moles of product per mol of $SnCl_4$).

Heterogeneous systems based on Sn(IV) embedded in zeolites, mesoporous silicas such as MCM-4 or hydrotalcite were found active (and selective) only towards cyclic ketones.[10d,10e,10g] Fe–Sn–O mixed oxides were tested[12f] only for cyclohexanone conversion; they showed high catalytic activity and selectivity for ε-caprolactone (98.8% yield, maintained in scale-up experiments).

Our optimized catalytic Sn systems are successfully applied to a much wider range of substrates. Moreover, they operate without co-catalysts, promoters or other additives.

It is believed that the reaction can occur by activation of the ketone as proposed for other cases,[10f,12a] upon coordination to the Sn centre, to nucleophilic attack by the hydrogen peroxide followed by heterolytic peroxo-bond cleavage and carbanion migration (Scheme 3).



Scheme 3 Proposed mechanism for the Baeyer-Villiger oxidation of ketones with hydrogen peroxide catalyzed by the Sn complex $[SnMe_2(HL)(CH_3OH)]_n.(0.5nCH_3OH)$ (**1**).

To investigate the recyclability of **1**, at the end of the reaction, the orange solid was recovered by filtration from the reaction mixture, thoroughly washed with methanol and dried overnight at 60 ºC. The subsequent cycle (up to five consecutive cycles) initiated upon addition of new standard portions of all other reagents. Under US conditions, **1** almost maintained its catalytic efficiency to convert selectively ketones during five consecutive cycles as illustrated for cyclopentanone in Fig. 5. In addition, catalyst **1** was verified by elemental analyses, IR spectra and X-ray powder diffraction studies before and after the catalytic reaction, and no significant changes were detected. This suggests a true heterogeneous catalytic activity for **1**.

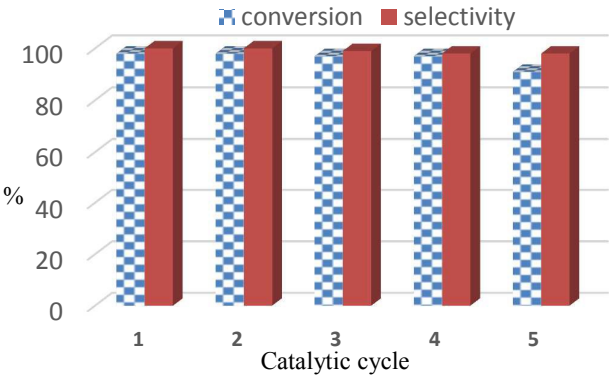


Fig. 5 Effect of the catalyst recycling on the yield of δ-valerolactonefor the US-assisted cyclopentanone oxidation (1 h) with H_2O_2, at 60 ºC, catalyzed by **1**.

MW-assisted conditions appear to be more aggressive, leading to a pronounced decomposition of **1** after the catalytic reaction (first cycle) with concomitant impairment of its recycling and re-use.

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Experimental

Materials and physical methods

All the reagents and solvents were purchased from commercial sources and used as received. The Schiff base H_3L was synthesized (by condensing the 2,3-dihydroxybenzaldehyde with 2-aminosulfonic acid) and characterized according to the reported procedure.[14g]

^{1}H (300 MHz), ^{13}C (75.45 MHz) and ^{119}Sn NMR spectra were run on a Bruker 300 MHz spectrometer using tetramethylsilane [$Si(CH_3)_4$] as internal reference. The infrared spectrum (4000–400 cm^{-1}) was recorded on a Bruker Vertex 70 instrument in KBr pellets (abbreviations: s = strong, m = medium and w = weak) while elemental (C, H and N) analysis was performed by the Microanalytical Service of the Instituto Superior Técnico. Mass spectrum (in DMSO+MeOH) was acquired on a Bruker HCT quadrupole ion trap equipped with an electrospray ion source using the following typical instrumental parameters: solution flow rate, 2.5 μL/min; ESI needle spray voltage, +4 kV; capillary exit voltage, −129 V; nebulizer gas pressure, 8 psi; dry gas flow rate, 4 L/min; dry gas temperature, 250 °C; octopole RF amplitude, 187 Vpp. The spectra were recorded in the range 100 – 1500 Da. Spectra typically correspond to the average of 20 – 35 scans.

The ultrasonic- or microwave-assisted BV reactions were carried out in an Elma Transsonic 600/H ultrasonic bath or in a focused Anton PaarMonowave 300 microwave reactor fitted with a rotational system and an IR temperature detector, respectively.

Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm). The temperature of injection was 240 ºC. The initial temperature was maintained at 80 ºC for 1 min, then raised 10 ºC/min up to 140 ºC (in the case of 3,3-dimethyl-2-butanone oxidation) or 180 ºC, and held at this temperature for 1 min. Helium was used as the carrier gas. The internal standard method was used to quantify the organic products. GC-MS analyses were performed at a Perkin Elmer Clarus 600 C instrument, equipped with a 30 m × 0.22 mm × 25 μm BPX5 (SGE) capillary column, and Helium (He) as the carrier gas. Reaction products were identified by comparison of their retention times with known reference compounds, and by comparison of their mass spectra to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

Synthesis

$[SnMe_2(HL)(CH_3OH)]_n\cdot(0.5nCH_3OH)$ (1): To a hot and stirred methanol (10 mL) suspension of H_3L (0.147 g, 0.5 mmol) was added dropwise a methanol solution (5 mL) of triethylamine (0.101 g, 1.0 mmol) affording a clear orange solution. Then, a methanol solution (5 mL) of [$SnMe_2Cl_2$] (0.110 g, 0.5 mmol) was added. After stirring for 20 minutes, the resulted dark orange solution was filtered and was kept at room temperature. After 4 h, dark orange crystals, suitable for X-ray diffraction analysis, formed which were collected by filtration and washed with cold methanol. Yield: 0.185 g (76%). $C_{16.5}H_{21}NSO_{6.5}Sn$ (488.12): calcd C 40.60, H 4.34, N 2.87%; found C 40.49, H 4.41, N 2.93%. IR data (KBr, cm^{-1}): ν(H_2O), 3436br; ν(C=N), 1639s; ν(C–O), 1257s; ν(sulfonate), 1384m. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): 10.36 (s, N–H); 9.26 (s, CH=N); 6.54–7.96 (m, 8-Ar-H); 1.18 (t, 6H, Sn–CH_3). ^{13}C NMR (75.45 MHz, DMSO-d_6, δ ppm): 161.2 (C_{imine}); 138.4–114.0 ($C_{aromatic}$); 8.9 (Sn–CH_3). ^{119}Sn NMR (300 MHz, DMSO-d_6, δ ppm): –192, –169. ESI-MS (m/z): 441 (100%) for $[SnMe_2(L)]^-$.

Crystal structure determination

The X-ray diffraction data of compound **1** were collected using a Bruker APEX-II PHOTON 100 with graphite monochromated Mo-Kα radiation. Data were collected using omega scans of 0.5º per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART[29a] software and refined using Bruker SAINT[29a] on all the observed reflections. Absorption corrections were applied using SADABS.[29a] Structures were solved by direct methods by using the SHELXS-2014 package[29b,c] and refined with SHELXL-2014.01.[29b,c] Calculations were performed using the WinGX System-Version 2014.01.[29d] All the hydrogen atoms attached to carbon atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation, while that attached to the $O_{methanol}$ and the N_{imine} atoms were located in the difference Fourier map and refined with isotropic vibration parameters 1.5 times the average thermal parameter of the parent atom, and with the help of distance restrains. A disordered methanol molecule was removed by SQUEEZE[29e] routine of PLATON[29f] and electron count (72) and void volume (340 $Å^3$) suggest four molecules of methanol per unit cell, thus half a molecule per asymmetric unit, which was confirmed by the elemental analysis. The solvent molecule was explicitly included in the final refinement. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for most of the remaining atoms were employed. The final refinement converged to R_1 ($I > 2\sigma(I)$) value of 0.0295. Related crystallographic data are included in Table 4.

Table 4 Crystallographic Data of **1**

Formula	$C_{16}H_{19}NO_6SSn\cdot0.5CH_3OH$
FW	488.09
Crystal colour	Orange
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	23.3403(10)
b/Å	11.8569(5)
c/Å	14.2652(6)
β/°	104.000(2)
V/$Å^3$	3830.5(3)
Z	8
T/K	303(2)
2*θ*/°	4.598–52.900
μ (Mo Kα)/mm^{-1}	1.478
ρ_{calcd}/g cm^{-3}	1.693
F(000)	1888
Absorption-correction	Multi-scan
Index ranges	–29<*h*<29

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	$-14<k<14$
	$-17<l<16$
Reflections collected	29887
Independent reflections	3919
R_{int}	0.0392
R_1[a]/ wR_2[b] [I > 2σ(I)]	0.0293/0.0714
R_1[a]/ wR_2[b] [for all F_o^2]	0.0383/0.0749
GOF on F^2	1.046

Procedure for the Baeyer-Villiger oxidation studies

Typically, the catalytic oxidation reactions of complex **1** were carried out neat in thermostated (r.t. to 60 ºC) Pyrex round bottom vessels immersed in an ultrasonic bath and in open atmosphere, or in sealed 5 mL capacity cylindrical Pyrex MW reaction tubes with a 10 mm internal diameter. The reaction vessel was charged with the required amount of catalyst for the desired (typically 1000:1) oxidant/catalyst molar ratio. Then, 2.0 mmol of ketone substrate and 2.0 mmol of H_2O_2 (30% aq. solution) were added, in this order, and the reaction mixture was (MW or US) irradiated for 15–60 min at the desired temperature. Then, 90 μL of cycloheptanone (internal standard) and 2.0 mL of diethyl ether (to extract substrate and organic products from the reaction mixture) were added. The products were analysed by ^{1}H NMR and GC (using the internal standard method) and their identification made by comparison with authentic samples.

Blank tests were performed, in a Sn-free system, for the different substrates and no products were detected. The catalytic activity of the sulfonated Schiff base H_3L was tested under the same conditions for cyclohexanone and no oxidation products were obtained.

Catalyst recyclability of **1** under the above different reaction conditions was investigated. Each cycle was initiated after the preceding one upon addition of new typical portions of all other reagents. After completion of each run, the products were separated for analysis (see above) and the catalyst was recovered (by filtration), washed with several portions of methanol and dried in oven overnight at 60 ºC.

Conclusions

We have synthesized a new dimethyltin(IV) based coordination polymer, $[SnMe_2(HL)(CH_3OH)]_n \cdot (0.5nCH_3OH)$ (**1**), utilizing as pro-ligand the multidentate Schiff base 2-[(2,3-dihydroxyphenyl)methylideneamino]benzenesulfonic acid (H_3L). Contrasting with the previously reported diethyl- and dibutyltin(IV) dinuclear derivatives, compound **1** is an organometallic coordination polymer forming 1D *zigzag* chains by means of bridging monodentate sulfonate groups. The chains of **1** are interlinked *via* H-bonding interactions to build a three dimensional polymeric association. To the best of our knowledge, this is the first dimethyltin(IV) polymer and the third organotin(IV) compound derived from a sulfonated Schiff base.

Besides the remarkably high selectivity achieved by the herein presented Baeyer-Villiger oxidation of ketones with hydrogen peroxide catalyzed by **1**, other attractive features are: easy catalyst recycling, very low catalyst loading (0.1 mol% *vs*. substrate), use of an aqueous oxidant, mild conditions, short reaction period and solvent- and additive-free protocol. Sonication proved to be the most convenient procedure, followed by the one with application of MW irradiation. The used microwave and sonochemical procedures are important steps towards the establishment of green chemical methods to synthesize esters and lactones, common intermediates with significance on the production of high valuable fine chemicals.

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Graphical Abstract

for

A Sulfonated Schiff Base Dimethyltin (IV) Coordination Polymer: Synthesis, Characterization and Application as a Catalyst for Ultrasound- or Microwave-Assisted Baeyer-Villiger Oxidation under Solvent-free Conditions

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The new dimethyltin(IV) coordination polymer $[SnMe_2(HL)(CH_3OH)]_n.(0.5nCH_3OH)$ (**1**), derived from 2-[(2,3-dihydroxyphenyl)methylideneamino]benzenesulfonic acid (H_3L), is an efficient heterogeneous catalyst for the peroxidative Baeyer-Villiger oxidation of ketones, under ultrasound or microwave irradiation and solvent- and additive-free conditions.