Diorganotin Salicylaldoximate Clusters: Their Fascinating Chemistry and Structures

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A large variety of small oxotin clusters, characterised as stable crystalline products or solution transients, has been obtained by the reaction of various diorganotin oxides and salicylaldoxime. The structures were investigated by high resolution multinuclear NMR methods and X-ray crystallography. The predominant trinuclear clusters contain one seven- and two five-coordinate tin atoms and undergo a series of reversible substitution reactions, including those leading to clusters of differing nuclearity, in solution at room temperature. Such a variety of structures is rather unusual in organotin chemistry.

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Introduction

An interesting review paper by White, Tasker and Smith[1] gives an overview of the crystal structural chemistry of phenolic oximes and their metal complexes. This review underlines that for both the free ligand and its metal complexes, hydrogen bonds between the oximic proton and

Marcel Gielen was born in Brussels in 1938. He received his PhD at the Université Libre de Bruxelles in 1963 with Professor Jacques Nasielski, in the field of the kinetics and mechanisms of the bimolecular electrophilic aliphatic substitutions. He was a fellow of the Fonds National de la Recherche Scientifique until he received a position of lecturer at the newly created Vrije Universiteit Brussel in 1966, where he became full professor in 1972. His main research interests were, and still are, the stereochemistry at carbon of S_E2 reactions at a saturated carbon atom, the fluxionality of inorganic and organometallic complexes, the stereochemistry of S_N2 reactions at tetrahedrally substituted atoms and the development of metal-based drugs. He is the author of 300 papers devoted to organometallic chemistry, devoted for instance to the synthesis, characterization and antitumour activities of organotin compounds. He has been the editor of several books and journals and is now, with Edward Tiekink, Narayan Hosmane and Rudolph Willem, the coordinating editor of the section "Main Group Metal Compounds" of Applied Organometallic Chemistry. He is, with Rudi Willem and Bernd Wrackmeyer, the editor of the series "Physical Organometallic Chemistry" published by Wiley; the fourth volume, Fluxional Organometallic Compounds, is in press. He is also, with Edward Tiekink, the editor of another book published by Wiley entitled "Metallotherapeutic Agents" that appears in 2004.

Monique Biesemans received her PhD in Organic Chemistry in 1978 at the Vrije Universiteit Brussel (VUB), where she studied the interaction between proteins and organic substrates by NMR spectroscopy under the supervision of Prof. Georges Van Binst. She worked since 1969 as assistant, and later as Doctor-Assistant at the VUB, under the leadership of Prof. Louis Van Hove, a specialist in steroid chemistry. In 1990, she joined the group of Prof. Marcel Gielen, where she directed her research to advanced structure determinations by multinuclear NMR spectroscopy, focussing on applied organotin chemistry, and more recently on organotin interface chemistry. She is the author or co-author of over 140 peer-reviewed publications on these subjects.

Rudolph Willem was born in 1948 and received his PhD in Theoretical Chemistry at the Université Libre de Bruxelles in 1975, active in group theoretical modelling of stereochemically dynamic processes under the supervision of Prof. Jean Brocas. He became assistant, and later Doctor-Assistant at the Vrije Universiteit Brussel (VUB) from 1972, under the leadership of Prof. Marcel Gielen. He is known as an active researcher in the field of experimental NMR applications on dynamic stereochemistry and in cellular NMR during a post-doctoral stay in the Max Planck Institute for Physiology in Dortmund, Germany, under the supervision of Prof. R. Kinne in 1987. He became an Associate Professor at the Engineering Science Faculty of the VUB from 1988, and the head of the NMR Department of the VUB from 1989. He received the titles Professor of Chemistry in 1997 and Full Professor and Vice-Dean of the Faculty in 2002. He is the author or coauthor of over 240 peer-reviewed publications on structural chemistry and advanced NMR applications to structure determinations, with focus on applied organotin chemistry, and more recently on organotin interface chemistry and tin NMR spectroscopy.

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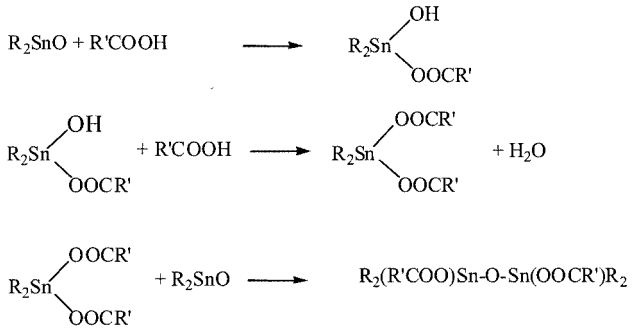
MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

phenolic oxygen atom play a fundamental role in the structural chemistry of these compounds. Whereas this review focuses on structures obtained from X-ray crystallography, the present review will be devoted, in the main, to the solution chemistry of tin salicylaldoximate clusters and will outline more particularly the existence of transient species generated upon dissolution (chloroform) of pure single crystals of these clusters. The use of 2D heteronuclear NMR techniques involving the ^{119}Sn nucleus is revealed as the optimal tool to investigate the structural chemistry of this system.

Many series of diorganotin carboxylates have been synthesized, either for investigating their solid state or solution structure,[2] or for assessing their performance as PVC stabilizers,[3] biocides,[4] anti-tumour agents,[5] anion-recognition agents,[6] and catalysts for polyurethane foams,[7] for room temperature vulcanisation of silicon rubbers,[8] for transesterifications,[9] for acetylations of alcohols,[10] and for dehydrations of alcohols to ethers.[11] They can be synthesized by condensing diorganotin oxides with carboxylic acids.[5] Two types of structures can be obtained, depending basically on the diorganotin oxide/carboxylic acid molar ratio. When a 1:1 ratio is used, dimeric dicarboxylatotetraorganodistannoxanes are generally generated through a diorganotin carboxylate hydroxide intermediate:



The latter compound dimerises as follows:

$$2\,[R_2(R'COO)Sn-O-Sn(OOCR')R_2] \rightarrow [R_2(R'COO)Sn-O-Sn(OOCR')R_2]_2$$

Moreover, a distannoxane unit can react with 2 equiv. of carboxylic acid to yield the diorganotin dicarboxylate:

$$R_2(R'COO)Sn-O-Sn(OOCR')R_2 + 2\,R'COOH \rightarrow H_2O + 2\,(R'COO)_2SnR_2$$

The dimeric centrosymmetric distannoxane is characterized by an Sn_2O_2 four-membered ring with two endocyclic five-coordinate tin atoms (quite common in organotin chemistry) that is linked, by the bridging oxygen atoms, to two exocyclic five-coordinate diorganotin moieties (Figure 1) so that the structure contains two μ_3-oxo functionalities.

When salicylaldoxime, represented hereafter as HOZNOH (see Scheme 1) rather than a carboxylic acid, is involved in condensation reactions with a diorganotin oxide,[12] a totally different coordination chemistry takes

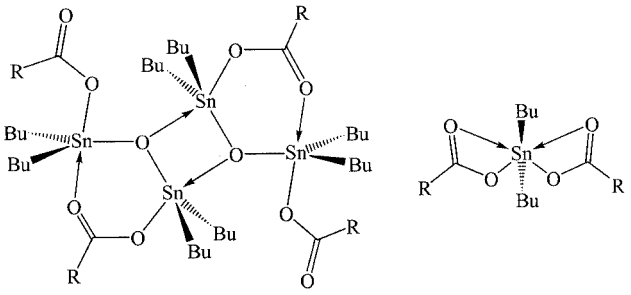
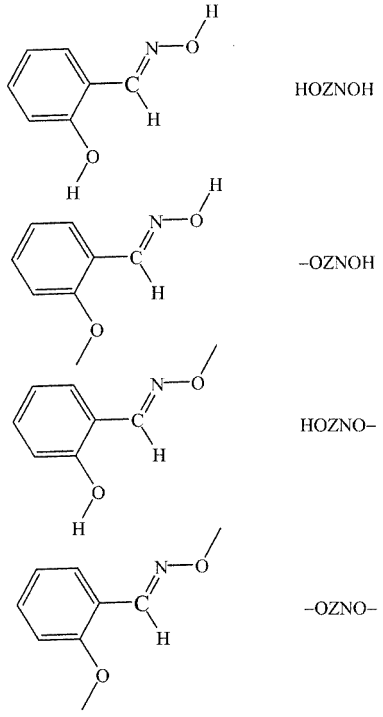


Figure 1. Structures of dimeric dicarboxylatotetraorganodistannoxanes and diorganotin dicarboxylates

place at the tin atom. This paper provides a review of the syntheses, structures and solution chemistry of tin salicylaldoximates, as investigated over the last decade or so.



Scheme 1

Structures and Chemistry of Diorganotin Salicylaldoximates

One of the reasons for the difference in the organotin chemistry of salicylaldoxime is the presence of two constitutionally different hydroxylic protons that can potentially be substituted by a metal atom. Reaction of salicylaldoxime with di-*n*-butyltin oxide gives rise to a cluster,[13–15] the structure[16] of which was determined by X-ray crystallography (see Figure 2) and investigated in solution by 1D and 2D multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR techniques.[16]

This complex is generated irrespective of the starting ratio between nBu$_2$SnO and HOZNOH, and can be formulated as [(Bu$_2$Sn)(Bu$_2$SnO)(Bu$_2$SnOH)(OZNO)(OZNOH)] (**1**). It contains a protonated distannoxane unit with two

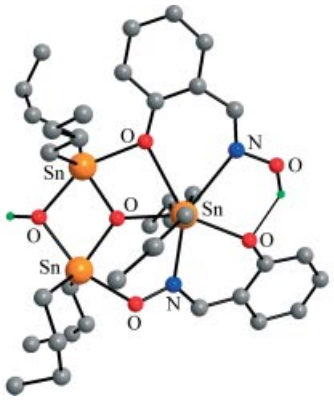


Figure 2. Structure of the crystalline organotin cluster $[(Bu_2Sn)(Bu_2SnO)(Bu_2SnOH)(OZNO)(OZNOH)]$ (**1**); in this diagram and in subsequent molecular structures, drawn with DIAMOND™, only the acidic hydrogen atoms are shown for reasons of clarity; colour code for all molecular structures in this review: orange, tin; red, oxygen; blue, nitrogen; turquoise, halide; grey, carbon; and green, hydrogen

five-coordinate tin atoms, which are in turn connected through a three-coordinate oxygen atom to a third, seven-coordinate tin atom, also coordinated by two differently bonded salicylaldoximate ligands. Another form (**1′**) related to cluster **1** arises from proton transfer from the SnOH moiety in the Sn_2O_2 group to the oxygen of the NO function of the OZNO ligand, as evidenced by ^{1}H NMR spectroscopy. The formula of **1′** is best represented as $[(Bu_2Sn)(Bu_2SnO)_2(OZNOH)_2]$ (see Figure 3).

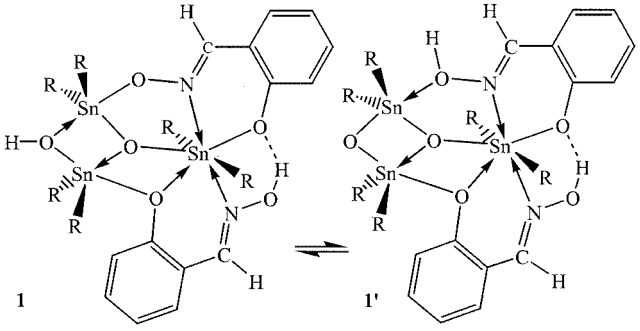


Figure 3. Structures in solution for the organotin cluster $[(Bu_2Sn)(Bu_2SnO)(Bu_2SnOH)(OZNO)(OZNOH)]$ (**1**) as found in the crystalline state, in equilibrium with a proton transfer isomer $[(Bu_2SnO)_2(Bu_2Sn)(OZNOH)_2]$ (**1′**)

In the latter formulation, a cyclodimer of diorganotin oxide is interacting with the one salicylaldoximate ligand through a PhO→Sn interaction and with the other one by a C=NO→Sn coordination, and an $(nBu_2Sn)_2O$→Sn contact from one oxygen atom of the four-membered Sn_2O_2 ring to the seven-coordinate tin atom. This suggests that the soluble cluster could act as an in situ reservoir of soluble diorganotin oxide, although this remains to be proven.[17,18]

Upon dissolution of monocrystalline **1** in $CDCl_3$, intense ^{119}Sn NMR resonances are observed for cluster **1**, together with other minor resonances that were assigned to other species as discussed below. Thus, a set of three minor, equally intense ^{119}Sn resonances were assigned to another cluster, **2**, that was subsequently synthesized independently from the reaction:

$$3\ HOZNOH + 3/n\ (R_2SnO)_n \rightarrow 2\ H_2O + [(R_2SnO)(R_2Sn)_2(HOZNO)(ZNOH)(OZNO)]\ (\mathbf{2})$$

Cluster **2** has three constitutionally different salicylaldoximate ligands. Its structural formula is shown in Figure 4, together with a crystal structure for the case when R = Me. Attempts to recrystallise **2** often failed for R = Me or provided crystals of **1** from undried solvents for R = *n*Bu. It was only under very carefully controlled crystallization conditions[19] that crystals of **2** could eventually be obtained for R = Me.

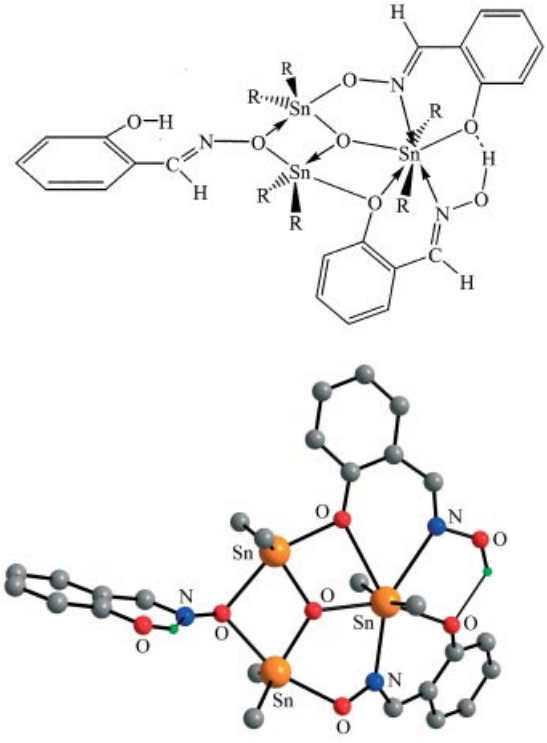


Figure 4. Lewis formula (top) and molecular structure (bottom) of the organotin cluster $[(R_2SnO)(R_2Sn)_2(HOZNO)(OZNOH)(OZNO)]$ (**2**; R = Me)

The μ_2-salicylaldoximate ligand of **2** is oriented in an approximately perpendicular position with respect to the almost planar trinuclear cluster. This yields a chiral skeleton in the solid state where the three tin atoms are inequivalent. The consequences of this chirality observed in the crystal are not observable in solution, suggesting a fast inversion of the skeletal chirality on the NMR timescale.[20]

The water generated in the synthesis of **2** is available in situ to convert **2** into **1**, which, at least for R = *n*Bu, explains the formation of the crystalline cluster **1** (Figure 2):

$$[(Bu_2SnO)(Bu_2Sn)_2(HOZNO)(OZNOH)(OZNO)] + H_2O \rightarrow [(Bu_2SnO)(Bu_2Sn)(Bu_2SnOH)(OZNOH)(OZNO)] + HOZNOH$$

The water converts the μ^2-bridging HOZNO ligand into the good nucleophilic leaving group HOZNOH in such a way so that the substitution reaction of the HOZNO ligand by HO can occur because it is catalysed through electrophilic assistance by a hydroxylic proton available in the medium (e.g. from water generated in situ and/or present in undried solvents).

The structures of **1** and **2** are quite similar, as can be deduced from the similarity of their tin NMR spectra as well as their crystalline structures. Both are unsymmetrical networks of tin−oxygen and tin−nitrogen bonds with one seven-coordinate tin atom and two five-coordinate tin atoms.

Another series of weak ^{119}Sn resonances arising upon dissolution of crystalline **1** originate from another totally different tin cluster, **3**, the structure of which, determined by multinuclear NMR spectroscopy, is shown in Figure 5. It contains two six- and two five-coordinate tin atoms and two salicylaldoximate moieties.

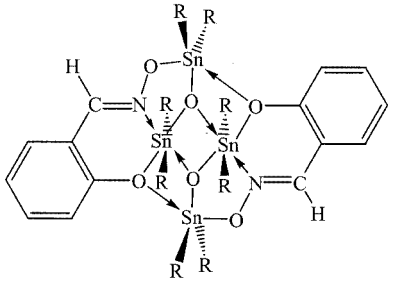


Figure 5. Structure of the organotin cluster $[(R_2Sn)_2(R_2SnO)_2(OZNO)_2]$ (**3**)

Lastly, a single ^{119}Sn resonance arises from a third very symmetrical cluster, **4** (Figure 6), containing four six-coordinate tin atoms and four salicylaldoximate ligands, as deduced from the relative intensities of $^2J(^{119}SnO\text{-}^{117}Sn)$ coupling satellites with respect to their parent signal.

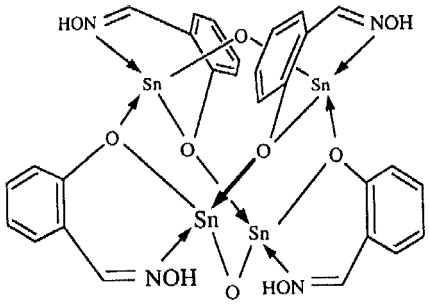


Figure 6. Structure of the organotin cluster $[(R_2Sn)_2(R_2SnO)_2(OZNOH)_4]$ (**4**); the tin-bound R groups have been omitted for clarity

An explanation for the formation of the first of the two minor species, $[(R_2Sn)_2(R_2SnO)_2(OZNO)_2]$ (**3**), observed in the solution generated from crystalline **1**, is shown in Figure 7:

$$2[(R_2SnO)(R_2Sn)(R_2SnOH)(OZNO)(OZNOH)] \rightarrow [(R_2Sn)(R_2SnO)(OZNOH)_2] + H_2O + 2[(R_2Sn)(R_2SnO)(OZNO)]$$

followed by

$$2[(R_2Sn)(R_2SnO)(OZNO)] \rightarrow [(R_2Sn)_2(R_2SnO)_2(OZNO)_2] \quad (3)$$

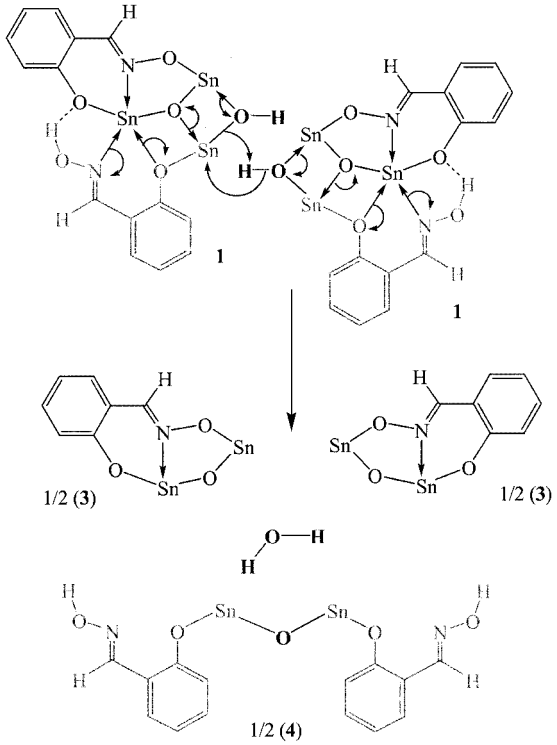


Figure 7. Reaction of two cluster units **1** yielding water, two identical molecules that, upon aggregation, provide **3**, as well as a distannoxane, the dimer of which is cluster **4**; the tin-bound R groups have been omitted for clarity

The second minor species, $[(R_2Sn)_2(R_2SnO)_2(OZNOH)_4]$ (**4**), is then formed by the dimerisation of $[(R_2Sn)(R_2SnO)(OZNOH)_2]$ generated by the reaction shown in Figure 7.

Another relatively straightforward reaction explains the presence of the latter minor compound **4**:

$$[(R_2Sn)(R_2SnO)(R_2SnOH)(OZNO)(OZNOH)] \rightarrow R_2SnO + [(R_2Sn)(R_2SnO)(OZNOH)_2]$$

which is again the monomeric precursor of **4**, R_2SnO precipitating in its usual polymeric form $(R_2SnO)_n$, in agreement with the experimental observation of precipitate formation.

Another reaction consistent with the presence of the minor species is given in Figure 8. Compound **1** can react with $[(R_2Sn)(R_2SnO)(OZNOH)_2]$ to yield $[(R_2SnO)(R_2Sn)_2(HOZNO)(OZNOH)(OZNO)]$ (**2**), H_2O

and $[(R_2Sn)(R_2SnO)(OZNO)]$, the monomeric precursor of **3**, already described above.

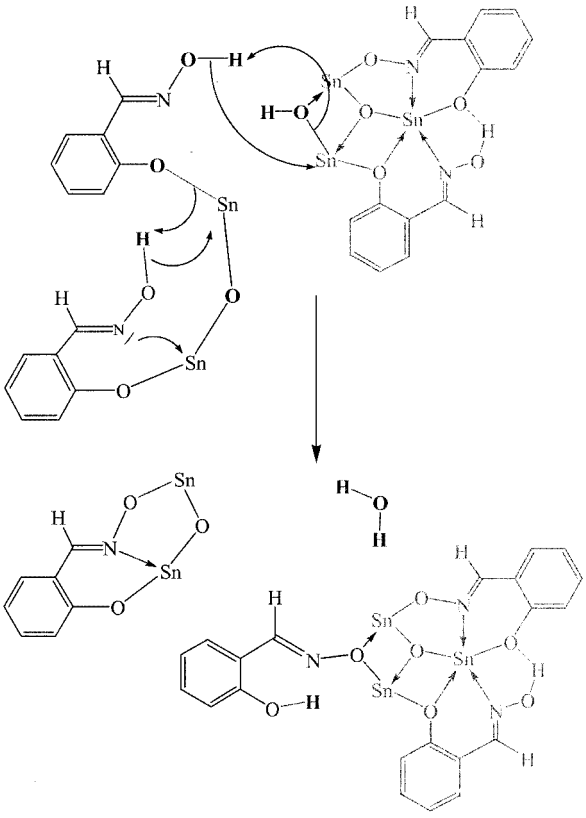


Figure 8. Reaction of cluster **1** with $[(R_2Sn)(R_2SnO)(OZNOH)_2]$, yielding water, cluster **2** and a distannoxane, the dimer of which is cluster **3**; the tin-bound R groups have been omitted for clarity

When both organic substituents on the tin atom are methyl groups, the dimethyl analogue of **1** can no longer be obtained in crystalline form. When alcohols R′OH are used for the crystallization, the crystals formed arise from novel structures containing an R′O group bridging the two five-coordinate tin atoms, instead of the OH group present in **1** (Figure 9),[21,22] i.e. $[(R_2Sn)(R_2SnO)(R_2SnOR')(OZNO)(OZNOH)]$ (see Table 1).

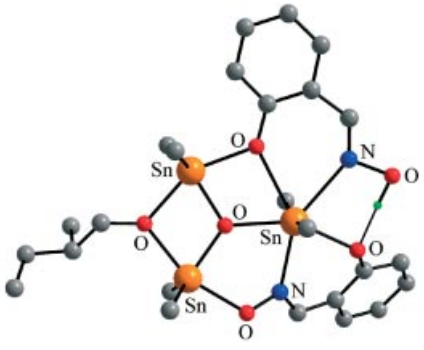


Figure 9. Structure of the organotin cluster $[(Me_2Sn)(Me_2SnO)(Me_2SnOCH_2CHMeEt)(OZNO)(OZNOH)]$ (**9**)

A mechanism similar to the one described for the transformation of **2** into **1** by the action of water remains applicable for the generation of **3** and **5**−**9** from **4**. This consists of protonation of the oximic oxygen atom of (HOZNO) in **4**, utilizing the proton from the entering R′OH to promote substitution with HOZNOH, which is the stable leaving group.

Table 1. Compounds obtained by treating di-*n*-butyl or dimethyltin oxide with salicylaldoxime; in the case when R = Me, compound **3** was observed solely as a transient, **4** was obtained as a crystalline solid, and compounds **5**−**9** were isolated from solutions in the corresponding alcohol R′OH

Compd.	R′O	R
1	HO	*n*Bu
2	*o*-HOZNO	*n*Bu
3	HO	Me
4	*o*-HOZNO	Me
5	MeO	Me
6	EtO	Me
7	PrO	Me
8	*i*PrO	Me
9	(*R*)-2-methylbutoxy	Me

More sterically hindered alcohols did not yield the corresponding alkoxy-bridged clusters. It should also be mentioned that the alkoxy-bridged compounds **5**−**9** are somewhat unstable since, upon ageing, their benzene solutions reveal the appearance of **4** and **3** as transients.

Because an electrophilic assistance by the proton of the entering R′OH appeared necessary in all these reactions to allow for the substitution of YO (YO = HOZNO or HO) by R′O, it was assessed whether other nucleophiles possessing a transferable proton are suitable for a similar substitution reaction. It appears that the MeO group of **5** can, indeed, be substituted for the PhCH=NO group (Figure 10),[22] yielding cluster **10**.

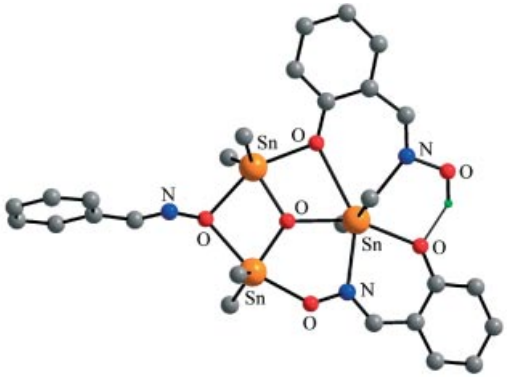


Figure 10. Structure of the organotin cluster $[(Me_2Sn)(Me_2SnO)(Me_2SnON{=}CHPh)(OZNO)(OZNOH)]$ (**10**)

Table 2 shows that phenols, ArOH, are also capable of inducing such reactions (Figure 11).[22]

Steric hindrance likewise hampers the substitution reaction in aryloxy cluster formation, as for the alkoxy cluster analogues, since 2,6-dimethylphenol, with a pK_a similar to the 3,5 analogue, is not capable of converting the methoxy

Table 2. Dimethyltin phenolate salicylaldoximato clusters synthesized from **5** and ArOH

Compd.	Ar
11	*p*-MeC_6H_4
12	*p*-BrC_6H_4
13	*m*-ClC_6H_4
14	*m*-$O_2NC_6H_4$
15	3,5-$Me_2C_6H_3$

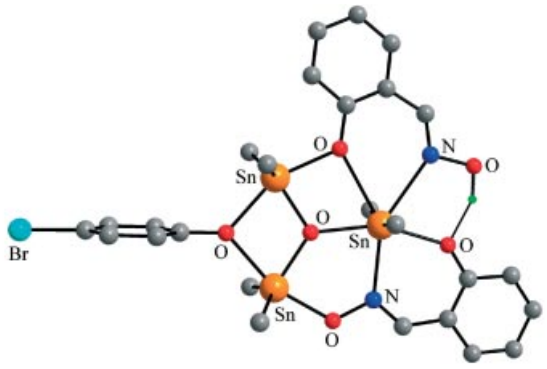


Figure 11. Structure of the organotin cluster [(Me_2Sn)(Me_2SnO)-($Me_2SnOC_6H_4$-*p*-Br)(OZNO)(OZNOH)] (**12**)

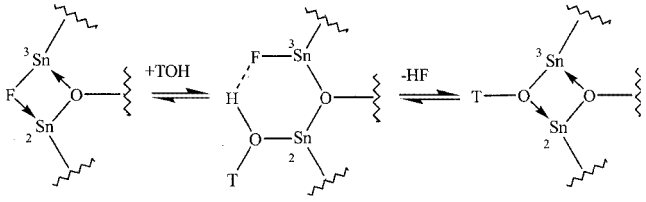
cluster into the corresponding 2,6-dimethylphenolate in pure form, as is the case with the 3,5 compound, **15**.

When treated with **5**, phenols with a pK_a slightly lower than 8.0, like *p*-cyanophenol (pK_a = 7.95) or *p*-nitrophenol (pK_a = 7.16), do not yield any substitution products that could be isolated as pure compounds, being observed solely as unstable transients. The threshold pK_a above which a substitution converts **5** into its aryloxy-substituted analogue in a way amenable to isolation and purification, lies in the range 8.0−8.4. Very acidic phenols, such as 2,4-dinitrophenol, completely destroy the cluster structure.

The acidity of carboxylic acids is also sufficient to destroy the cluster skeleton, yielding the usual carboxylatodistannoxane dimers discussed in the Introduction. However, the low acidity of the nucleophile is not sufficient to allow for a smooth substitution, since the weakly acidic acetylacetone (acacH) converts **5** into [$Me_2Sn(acac)_2$]. When **5** is treated with ethylene glycol, 2,2-dimethyl-1,3-dioxa-2-stannacyclopentane is generated.

A special case is provided by cluster **16** (Figure 12)[23] where the nucleophile bridging both five-coordinate tin atoms is simply a fluoride ion. Cluster **16** was obtained by reaction of **4** with NH_4F, showing that the necessary acidic reaction activation is ensured by a proton of the ammonium cation being transferred to the bridging HOZNO ligand to be substituted as HOZNOH. The mechanism of the substitution reaction of fluoride towards **4** or **5** was completely elucidated, taking advantage of the benefits of ^{19}F and ^{119}Sn NMR spectroscopy, in particular the associated spectral patterns arising from $^1J(^{19}F\text{-}^{119/117}Sn)$ scalar couplings. It was unambiguously established that the substitution occurs through an addition/elimination reaction mechanism, involving an intermediate where the entering and leaving nucleophiles are part of a motif where the transferred proton acts as a hydrogen bond connecting them (see Scheme 2).

Figure 12. Structure of the organotin cluster [(Me_2Sn)(Me_2SnO)-(Me_2SnF)(OZNO)(OZNOH)] (**16**)



Scheme 2

Conclusion

It can be stated that a large variety of small clusters can be obtained as stable crystalline products or solution transients upon reaction between diorganotin oxides and salicylaldoxime. The basic coordination pattern consists of one seven- and two five-coordinate tin atoms. In solution, such clusters undergo readily reversible substitution reactions under very mild conditions revealing a very broad panel of novel clusters. This variety is rather unusual in organotin chemistry.

Acknowledgments

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