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An Organotin Vanadate with Sodalite Topology and Catalytic Versatility in Oxidative Transformations

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The new coordination polymer formulated as [Et₃SnVO₃] (1) has been synthesized and shown by a combined single-crystal and synchrotron powder X-ray diffraction structural analysis, supported by solid-state NMR, to possess a three-dimensional network structure with the sodalite topology, formed by tetravanadate polyanions, $[V_4O_{12}]^{4-}$, that are linked by Et₃Sn⁺ spacers. The catalytic versatility of compound 1 for liquid phase organic reactions was demonstrated by applying it for the epoxidation of olefins, the oxidative dehydrogenation of alcohols, and the oxidation of benzyl alcohol to benzaldehyde

Introduction

It is well known that homogeneous (molecular) catalysts containing early transition metals (Ti, V, Mo, W and Re) in high oxidation states (IV–VII) can selectively catalyze various types of liquid-phase oxidation reactions such as sulfoxidation and olefin epoxidation.^[1] The most effective catalysts are metal-organic complexes in which the active metal center is surrounded by organic (and inorganic) ligands. Vanadium complexes have been found to be particularly efficient catalysts in the oxidation of C–H compounds and olefins by H₂O₂ and other peroxides.^[1c,2] Researchers have sought the installation of these active sites within the backbone of metal-organic hybrids (especially metal-organic frameworks (MOFs) or, more widely speaking, coordina-

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This manuscript is part of a Special Issue on the "Portuguese Conference on Catalysis" based on the International Symposium on Synthesis and Catalysis (ISySyCat). and benzoic acid, using *tert*-butyl hydroperoxide (TBHP) as oxidant. Compound **1** acts a solid reservoir for soluble, catalytically active species, which promote high selectivities to the epoxide and carbonyl (aldehyde/ketone/acid) products. The epoxidation activity compares favorably with those reported for other organotin molybdate, tungstate and vanadate coordination polymers, and is superior to that displayed by the starting materials used for its synthesis (Et₃SnBr and NH₄VO₃) and the metavanadate NBu₄VO₃.

tion polymers) with the goal of obtaining self-supported or heterogeneous catalysts.^[3] MOFs are multidimensional coordination networks comprised of inorganic secondary building units (SBUs, metal ions or clusters) spatially separated by organic linkers. A few vanadium-based MOFs are known and one of these, V-MIL-57, was shown to be capable of high activity and selectivity in the epoxidation of cyclohexene with tert-butyl hydroperoxide (TBHP).^[3a-c] The structure of thermallyactivated V-MIL-47 consists of $\{V^{IV}-O-V^{IV}\}_{\infty}$ chains of cornersharing {VO₆} octahedra, which are cross-linked by terephthalate linkers. Related (albeit non-porous) three-dimensional (3D) molybdenum oxide-organic frameworks have been prepared by the linkage of 1D Mo^{VI} oxide motifs through suitable bistriazolyl ligand modules.^[4a,b] These compounds were used as (pre) catalysts for the epoxidation of cis-cyclooctene, the oxidative dehydrogenation of benzyl alcohol, and the oxidation of benzaldehyde.^[4b,c]

All of the metal-organic hybrids referred to above contain organic linkers. The use of organometallic bridging ligands to construct metal-organometallic frameworks and coordination polymers is an underdeveloped area^[5] and catalytic applications have yet to be broadly studied despite the potential synergistic benefits of an ordered heterobimetallic system.^[6] One family of materials that have attracted attention in this regard are triorganotin molybdates, tungstates and vanadates, in which R_3Sn^+ moieties connect either tetrahedral MO_4^{2-} groups (M = Mo, W) or $\{V^V\text{-}O\text{-}V^V\}_\infty$ chains to form 1D, 2D or 3D network structures. The structures are very much dependent on the nature of the substituent R and the Sn/M molar ratio ($M = V_r$, Mo, W).^[7] With R = Me, M = Mo (or W) and Sn/M = 1, anionic coordination polymers of the type [(Me₃Sn)MO₄]⁻ are formed in which Me₃SnO₂ bipyramides are linked with MO₄ tetrahedra to form chains.^[8] For Sn/M = 2, i.e. [(Me₃Sn)₂MO₄], all four of the Mbonded oxygens are linked to Me₃Sn⁺ groups, resulting in a



layered structure.^[9] Catalytic investigations with these compounds were first described by Abrantes, Gonçalves and Romão and co-workers.^[10] The 2:1 derivatives $[(R_3Sn)_2MO_4]$ (M = Mo, W; R=methyl, n-butyl, cyclohexyl, phenyl, benzyl) were examined for the oxidation of benzothiophene^[10a] and the epoxidation of olefins.^[10b,c] Catalytic performance was strongly affected by the nature of M and the tin-bonded R groups, the type of oxidant used (H₂O₂ or TBHP), and the addition of cosolvents. One of the most catalytically active systems for both reactions comprised the tri-n-butyltin molybdate as catalyst, aqueous H₂O₂ as oxidant and a chlorinated cosolvent. The compounds [(nBu₃Sn)₂ MO_4] (M = Mo, W) were subsequently used as recyclable heterogeneous catalysts for the oxyfunctionalization of monoterpenes,^[11] N-oxidation of primary and secondary amines,^[12] and the synthesis of hexahydroquinoline and 1,4-dihydropyridine derivatives.[13] The high activity and selectivity of $[(nBu_3Sn)_2MoO_4]$ for the transesterification of diethyl carbonate and various alcohols was attributed to a synergistic effect between the groups of MoO_4^{2-} and Bu_3Sn^+ in the catalyst.^[14]

Catalytic studies with the trimethyltin vanadate $[Me_3SnVO_3]$ indicated that it was a more efficient catalyst than $[(nBu_3Sn)_2 MOO_4]$ for the epoxidation of olefins with TBHP.^[15] The trimethyltin vanadate has a 3D network structure comprising infinite metavanadate chains which are linked by Me_3Sn^+ cations.^[16] Given that the tin-bonded R groups in organotin metalates have a strong structure-directing (and hence catalytic) influence, we undertook the synthesis of the triethyltin analogue, [Et₃SnVO₃], which has not been previously reported. Herein we describe the structural elucidation of this compound and an examination of its catalytic performance for the epoxidation of olefins and the oxidation of alcohols.

Results and Discussion

Synthesis and Structural Elucidation

The organotin vanadate $[Et_3SnVO_3]$ (1) was obtained in nearquantitative yield as an analytically pure pale yellow polycrystalline precipitate after addition of an acetone solution of Et_3SnBr to a solution of NH_4VO_3 in water [Eq. (1)].

$$NH_4VO_3 + Et_3SnBr \xrightarrow{H_2O/Me_2CO} [Et_3SnVO_3] (1) + NH_4Br$$
(1)

The vanadium (V⁵⁺) environment in **1** was investigated by ⁵¹V MAS NMR spectroscopy (Figure S1 in the Supporting Information). A single isotropic peak is observed at $\delta = -666.3$ ppm, indicating the existence of one type of V⁵⁺ site. Similarly, the presence of one type of Et₃Sn group is indicated by the ¹¹⁹Sn HPDEC MAS NMR spectrum, which shows one fairly sharp resonance at $\delta = 74.3$ ppm, and the ¹³C{¹H} CP MAS NMR spectrum, which shows two peaks at $\delta = 10.5$ and 12.6 ppm for the Sn-bonded ethyl groups (Figure S1). These results point to the presence of single crystallographically unique V and Sn sites in the crystal structure of **1**. Although the crystal structure solution shows that the three CH₂ and three CH₃ groups in each Et₃Sn⁺ cation are not crystallographically equivalent (see

below), their chemical equivalence together with considerable structural disorder account for why only single peaks are observed for each type of carbon atom.

The IR and Raman spectra of compound 1 are consistent with the presence of cyclic tetranuclear $[V_4O_{12}]^{4-}$ clusters in the structure (Figure S2). In the Raman spectrum, the bands at 953 and 918 cm⁻¹, with strong and medium intensity, respectively, may be assigned to symmetric stretching vibrations, $v_{sym}(VO_2)$, of the two shortest V-O (terminal V=O character) bonds, i.e. those linked to Et₃Sn⁺ cations. The same modes appear to originate weak-medium IR bands at 963 and 913 cm⁻¹. These assignments are made on the basis of previous assignments made for the tetrametavanadate anion.^[17] According to these previous assignments, the very strong band at 807 cm⁻¹ in the IR spectrum of 1 is due to the IR-active mode arising from the asymmetric stretching of these groups, $v_{asym}(VO_2)$; the weak Raman band at 863 cm⁻¹ may be due to the Raman-active component arising from this mode. A strong band due to a V–O–V stretching mode, v_{asym} (V–O–V), is found at 672 cm⁻¹ in the IR spectrum. In the region of the V–O stretching vibrations the IR spectrum of 1 closely resembles those reported previously for several hybrid materials containing metalphenanthroline complexes and [V₄O₁₂]⁴⁻ rings.^[18] Žúrková et al. proposed slightly different band assignments, namely $v_{sym}(VO_2)$ and $v_{asym}(VO_2)$ for the high-frequency (>900 cm⁻¹) bands, v_{asym} (V–O–V) for the band around 810 cm⁻¹, and v_{sym} (V–O–V) for the band around 670 cm⁻¹.^[18]

For 1, the Raman-active ν (SnC) vibration appears at 486 cm⁻¹ and is in agreement with literature results for the coordination polymer [(Et₃Sn)₃Co(CN)₆].^[19] A second, considerably weaker, Raman band at 523 cm⁻¹ is assigned to one of the asymmetric (with respect to the SnC₃ fragment) stretching modes which appears more clearly in the IR spectrum at the same frequency.^[19]

A full structure description of 1 was achieved through a combination of single-crystal and synchrotron high-resolution powder X-ray diffraction (XRD) studies. Single-crystals were obtained by dissolving 1 in DMF, followed by layering the resultant solution with pentane (middle layer) and diethyl ether (top layer). The compound crystallizes in the cubic F-43c space group (Table 1), exhibiting a considerable structural disorder for the Sn-bound ethyl moieties, and some solvent accessible volume that could not be unequivocally modelled because of a considerable smeared-out electron density. The homogeneity of the bulk material was unequivocally confirmed from Rietveld refinement using high-resolution powder XRD data as depicted in Figure 1. The combined study clearly shows that the presented model describes well the structural features of 1, with the missing electron density contributing mostly to the overall background of the XRD data.

The asymmetric unit of **1** is composed of just two metal centers as shown in Figure 2. Sn1 exhibits a distorted $\{SnC_3O_2\}$ trigonal bipyramidal coordination environment in which the equatorial plane is formed by the disordered ethyl moieties and the apical positions are occupied by oxygen atoms from $[V_4O_{12}]^{4-}$ tetrameric units [internal polyhedral angle close to being linear - 178.5(9)°]: while the Sn–O distances were found



Table 1. Crystal and structure refinement data for [Et ₃ SnVO ₃] (1).				
Formula	$C_6H_{15}O_3SnV$			
Formula weight	304.81			
Crystal system	Cubic			
Space group	F-43c			
a [Å]	30.565(4)			
Volume [ų]	28554(10)			
Z	96			
$D_{\rm c} [{\rm g}{\rm cm}^{-3}]$	1.702			
μ (Mo-K α) [mm ⁻¹]	2.853			
Crystal size [mm]	0.31×0.28×0.21			
Crystal type	Yellow block			
θ range	3.77 to 25.35			
Index ranges	$-36 \le h \le 21, -35 \le k \le 29, -35 \le l \le 13$			
Reflections collected	16543			
Independent reflections	2132 [R _{int} =0.0594]			
Completeness to $\theta = 25.24^{\circ}$	97.5%			
Final <i>R</i> indices $[I > 2\sigma(I)]^{[a,b]}$	R1=0.0742, wR2=0.1913			
Final <i>R</i> indices (all data) ^[a,b]	R1 = 0.0937, wR2 = 0.2103			
Weighting scheme ^[c]	m = 0.1390			
Largest diff. peak and hole	2.115 and -0.477 eÅ ⁻³			
$\boxed{\begin{bmatrix} a \\ R1 = \sum \left\ F_o \right - \left F_c \right\ / \sum \left F_o \right }$				

[b] $wR2 = \sqrt{\sum \left[w \left(F_o^2 - F_c^2 \right)^2 \right] / \sum \left[w \left(F_o^2 \right)^2 \right]}$ [c] $w = 1 / \left[\sigma^2 \left(F_o^2 \right) + \left(mP \right)^2 + nP \right]$ where $P = \left(F_o^2 + 2F_c^2 \right) / 3$

Table 2. Bond distances (in Å) and angles (in degrees) for the distorted
trigonal bipyramidal {SnC ₃ O ₂ } coordination environment and the tetrahe-
dral V ⁵⁺ site in [Et ₃ SnVO ₃] (1). ^[a]

	5 5 4 7				
Sn1–O1 Sn1–O3 ⁱ	2.204(8) 2.311(10)	01–Sn1–O3 ⁱ V1–O1–Sn1 V1 ⁱⁱⁱ –O2–V1 V1–O3–Sn1 ^{iv}	178.5(9) 141.0(5) 160.9(8) 156.3(9)		
Disordered carbon 83(2) %	n atoms (see Figu	re 2 for details):			
Sn1–C1 Sn1–C5 Sn1–C7 C1–Sn1–O1 C5–Sn1–C1 C5–Sn1–C1 C5–Sn1–O1 C7–Sn1–C1 C7–Sn1–C5 C7–Sn1–O1 C7–Sn1–O1 C7–Sn1–O3 ⁱ	2.145(12) 2.145(12) 2.145(12) 97.7(10) 81.9(9) 117.2(12) 88.9(11) 92.5(10) 105.8(12) 136.2(12) 93.0(10) 85.7(9)	Sn1-C2 Sn1-C4 Sn1-C8 C2-Sn1-O1 C2-Sn1-O3 ⁱ C4-Sn1-C2 C4-Sn1-O3 ⁱ C8-Sn1-C4 C8-Sn1-C4 C8-Sn1-C2 C8-Sn1-O1 C8-Sn1-O3 ⁱ	2.145(12) 2.145(12) 2.145(12) 109(3) 72(2) 112.5(19) 90(2) 91(2) 109.7(16) 135(3) 85.0(16) 93.5(16)		
V1-01 V1-02 ⁱⁱ V1-02 V1-03	1.659(8) 1.711(19) 1.736(19) 1.593(10)	01-V1-02 01-V1-02 ⁱⁱ 02 ⁱⁱ -V1-02 03-V1-01 03-V1-02 03-V1-02 ⁱⁱ	109.7(16) 109.6(17) 107.5(7) 106.9(5) 115.4(16) 107.6(14)		
[a] Symmetry transformations used to generate equivalent atoms: (i) y , - $x+1.5$, - $z+2$; (ii) - $x+1.5$, $z-0.5$, - $y+1.5$; (iii) - $x+1.5$, - $z+1.5$, $y+0.5$; (iv) - $y+1.5$, x , - $z+2$.					

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in the 2.204(8)-2.311(10) Å range, all Sn–C bond lengths are identical to 2.145(12) Å (see Table 2 for details – this occurs because of the structural constraints imposed in the single-crystal XRD modeling so as to ensure chemically reasonable geometries for these disordered moieties). The structural model has one position for the ethyl groups significantly more favored with a rate of occupancy of 83(2) %. We emphasize that this may change from crystal to crystal since for the powder XRD studies the rates had to be slightly adjusted to a ratio of *ca*. 3 : 2 to better fit the data. V1 exhibits a typical tetrahedral {VO₄} coordination environment with the V–O distances ranging from 1.593(10) to 1.736(19) Å, and the tetrahedral internal angles from 106.9(5) to 115.4(16)° (Table 2). This tetrahedral building unit is corner-shared with three symmetry-related ones to form a $[V_4O_{12}]^{4-}$ tetrameric moiety as depicted in Figure 2b and 2d.

The crystal structure of 1 is constructed by bridges between $[V_4O_{12}]^{4-}$ tetrameric moieties via the distorted {SnC₃O₂} trigonal bipyramidal Sn environments, ultimately forming a supramolecular cage as depicted in Figure 3a. These connections are ensured by the O1 and O3 oxygen atoms of the crystallographically independent {VO₄} coordination environment, which imposes some local stress in the overall geometry which is ultimately reflected by the smallest tetrahedral O3–V1–O2 angle of 115.4(16)° (Figure 2b and Table 2). The $\{[Et_3Sn]_{12}[V_4O_{12}]_6\}^{12-}$ supramolecular cage (the -12 charge arises because this formula accounts for a total of 24 fully-occupied inter-cage connecting oxygen atoms) contains empty space at the center which is most likely occupied by solvent molecules. As shown in Figure 3a, this void is surrounded by ethyl groups and, therefore, is of hydrophobic nature. The impossibility of establishing strong supramolecular interactions with the eventually confined solvent molecules further explains the smearedout electron density registered in the XRD studies.

The interconnection between $[V_4O_{12}]^{4-}$ tetrameric moieties and the bridging Et₃Sn⁺ spacers leads to the formation of a truly unprecedented, high-symmetry 3D hybrid network as depicted in the inset of Figure 1. A search in the literature and in the Cambridge Structural Database (CSD Version 5.38 with 3 updates)^[20] reveals the existence of only a handful of organotin vanadate compounds in the literature. Although the majority are discrete complexes,^[21] a number of polymeric structures have also been reported: two 1D chain-type polymers reported by Herntrich & Merzweiler ([(Ph₃Sn)₃VO₄]·CH₃CN and [(Ph₃Sn)₃ VO₄]·2DMF);^[22] two 3D compounds (just like 1) originally described by Rosenland & Merzweiler ([Me₃SnVO₃] and $[(Me_2Sn)_4V_2O_9])_{1}^{[16]}$ with the former being more recently redetermined and studied by us.^[15] In this context, compound 1 stands out as a truly unique material with a topology similar to that of a known mineral (see below). The Sn-bound organic moiety seems to have some influence on the isolated structure: while bulky ligands such as phenyl seem to promote the formation of low-dimensional structures (i.e., 1D), aliphatic ligands allow the polymerization into 3D frameworks; in addition, although the number of comparable structures is small, one can infer that the size of small aliphatic chains (methyl or ethyl groups) does not have any influence on this type of dimensionality since for both cases 3D frameworks were isolated.



Figure 1. Final Rietveld plot (synchrotron XRD data) of $[Et_3SnVO_3]$ (1) (Debye-Scherrer geometry, 2θ range: 1.000-22.000, 110 K). Observed data points are indicated as a blue line, the best fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid red and grey lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections for 1. The inset depicts a perspective view along the [100] direction of the unit cell

of 1. Refinement details: Zero shift $[2\theta^{\circ}] = -0.006(2)^{\circ}$; 344 independent reflections; 36 global refined parameters; $R_p = \frac{\sum_{i} |y_{i,o} - y_{i,c}|}{\sum_{i} |y_{i,o}|} = 8.06$; $R_{wp} = \sqrt{\frac{\sum_{i} w_i(y_{i,o} - y_{i,c})^2}{\sum_{i} w_i(y_{i,o})^2}} = 7.72$; $R_{exp} = \sqrt{\frac{\sum_{i} (n-p)}{\sum_{i} w_i(y_{i,o})^2}} = 5.08$; $GOF = \frac{R_{up}}{R_{up}} = 1.52$; $R_{Bragg} = \frac{\sum_{i} |y_{i,o} - y_{i,c}|}{\sum_{i} h_{o,o}} = 7.13$ where $y_{i,o}$ and $y_{i,c}$ are the observed and calculated profile

intensities, $I_{n,o}$ and $I_{n,c}$ the observed and calculated intensities, respectively. The summations run over *i* data points or *n* independent reflections. Statistical weights *wi* are usually taken as $1/y_{i,o}$.



Figure 2. Schematic representation of the (a) Sn⁴⁺ and (b) V⁵⁺ crystallographically independent coordination environments present in $[Et_3SnVO_3]$ (1) resembling, respectively, a distorted trigonal bipyramid and a distorted tetrahedron. (c) and (d) Top views of the same {SnC₃O₂} and {VO₄} coordination environments. Selected bond lengths and angles are given in Table 2. Symmetry transformations used to generate equivalent atoms have been omitted for clarity.

Following the recommendations of Alexandrov *et al.*,^[23] who suggested that any moiety (ligand, atom or clusters of atoms) connecting more than two metal centers (μ_n) should be considered as a network node, **1** is a uninodal 4-connected network (node: the V⁵⁺ metal center) with a Schäfli point symbol of {4²·6⁴} as revealed by the software package TOPOS.^[24] As represented in Figure 3b, the internodal distances vary between 3.399(5) Å (for the V…V distance within the [V₄O₁₂]⁴⁻ tetrameric moieties) and 7.450(3) Å (for the bridge across the Et₃Sn⁺ spacers). Remarkably, **1** shares the topology with the well-known mineral sodalite (sod), with the crystal structure (inset in Figure 1) being described by the close packing of sodalite-like cages as shown in Figure 4.

The thermal stability of compound **1** was studied by thermogravimetric analysis under air (Figure S3 in the Supporting Information). Decomposition of the Sn-bonded ethyl groups begins at 160 °C and leads to a very abrupt ($DTG_{MAX} = 210$ °C) mass loss of 19.8% up to 220 °C, followed by a more protracted loss of about 10% in overlapping steps between 220 and 500 °C.

Investigation of the particle morphology of **1** by scanning electron microscopy (SEM) revealed aggregates of irregular flakelike particles (Figure S4 in the Supporting Information).





Figure 3. (a) Schematic representation of the sodalite-like $\{[Et_3Sn]_{12}[V_4O_{12}]_6\}^{12-}$ supramolecular cage formed by the interconnection between corner-shared tetramers, $[V_4O_{12}]^{4-}$, and Et_3Sn^+ spacers. (b) Simplified topological construction of the same sodalite-like cage in which the μ_2 bridges formed by the Et_3Sn^+ spacers have been removed [internodal distance of 7.450(3) Å].



Figure 4. Crystal packing of cubic $[Et_3SnVO_3]$ (1) represented by the interconnection between adjacent sodalite-like cages. Representation created using the software package Systre.^[25]

Catalytic Studies

The catalytic performance of **1** was investigated for the epoxidation of *cis*-cyclooctene (Cy8) with TBHP, without cosolvent, at 55 °C. Cyclooctene oxide (CyO) was the only product formed with 82% yield at 24 h reaction (Table 3). This performance is on a par with those reported previously for organotin molybdates $[(R_3Sn)_2MoO_4(H_2O)_n]$ ($R_3 = (Me)_2(menthyl)$ or *n*Bu₃) used under equivalent reaction conditions (Table 4).^[10b,26] The trimethyltin vanadate [Me₃SnVO₃] led to a slightly lower epoxide yield of 65% at 24 h for the Cy8 reaction with TBHP.^[15] Compound **1** exhibited superior catalytic performance to the starting materials used for its synthesis (Et₃SnBr, negligible Cy8 conversion; NH₄VO₃, 1% CyO selectivity at 32% conversion) and the metavanadate NBu₄VO₃ (84% CyO selectivity at 42% conversion). These results suggest that the active species of **1** contain vanadium(V) in a favorable coordination

Table 3. Reactions of olefins and alcohols with TBHP in the presence of 1, at 55 $^\circ\text{C}.$					
Substrate	Cosolvent	Conv. [%] ^[a]	Select. [%] ^[b]		
Olefins					
<i>cis</i> -cyclooctene	none	82 (82) ^[c]	100 (100) ^[c]		
	1,2-dichloroethane	78	100		
	hexane	73	100		
	acetonitrile	65	100		
cyclododecene	none	65	93		
1-octene	none	23	100		
trans-2-octene	none	45	100		
(R)-(+)-limonene	none	68	85 ^[d]		
α-pinene	none	50	67		
Alcohols					
cyclooctanol	none	68	94		
cyclohexanol	none	55	100		
1-cyclohexylethanol	none	45	96		
sec-phenethyl alcohol	none	62	98		
benzyl alcohol	none	78	24		

^[a] Substrate conversion at 24 h reaction. ^(b) Selectivity to the corresponding epoxide in the case of the olefins, and carbonyl (aldehyde/ketone) products in the case of the alcohols. ^[c] Catalytic results in parentheses are for the used catalyst. ^[d] Selectivity to 1,2-limonene oxide. The corresponding 1,2-epoxide, 8,9-epoxide and 1,2:8,9-diepoxide products were formed in a molar ratio of 1:0.09:0.09.

Table 4. Cyclooctene epoxidation in the presence of organotin metalate compounds. $^{[a]}$							
Cy8 [M]	Cat. Load $[g_{cat} L_{mix}^{-1}]$	MR	Conv. [%] ^[b]	Ref.			
3.6	5.7	1:130:200	82	This work			
3.5	2.3	1:400:640	65	[15]			
3.7	19.1	1:100:150	~85	[26]			
2.7	15	1:100:200	88	[10b]			
2.7	16.7	1:100:200	30	[10b]			
	Cy8 [M] 3.6 3.5 3.7 2.7 2.7	Cy8 Cat. Load [M] $[g_{cat} L_{mix}^{-1}]$ 3.6 5.7 3.5 2.3 3.7 19.1 2.7 15 2.7 16.7	Cy8 Cat. Load MR $[M]$ $[g_{cat}L_{mix}^{-1}]$ MR 3.6 5.7 1:130:200 3.5 2.3 1:400:640 3.7 19.1 1:100:150 2.7 15 1:100:200 2.7 16.7 1:100:200	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			

^[a] Reaction conditions: oxidant = 5.5 M TBHP in decane, 55 °C, no cosolvent. Other experimental conditions shown for comparison are initial molar concentration of Cy8, catalyst load (expressed as initial mass of organotin compound per total volume of reaction mixture), and initial catalyst:-Cy8:TBHP molar ratio (MR). ^[b] Cy8 conversion at 24 h. Epoxide selectivity was 100% in all cases. ^[c] $R_3Sn = (Me)_2(menthyl)Sn$.

environment for the catalytic epoxidation reaction. The reaction mechanism may involve the coordination of the Lewis base hydroperoxide oxidant to the Lewis acid metal center (activating the peroxidic oxygen atom), and an oxygen atom transfer reaction from the oxidizing species to the olefin.^[27]

The addition of a cosolvent to the reaction mixture affected the catalytic performance of 1 (Figure 5, Table 3): the reaction rate (based on conversion at 50 min reaction) decreased in the order: no cosolvent (29%) > 1,2-dichloroethane (19%) \approx hexane (17%) > CH₃CN (8%). Possibly, the catalyst's acidity is levelled off by the Lewis basic CH₃CN and/or these molecules compete with the reagents for coordination to the metal center, leading to slower reaction kinetics.

The olefin substrate scope was expanded to other cyclic and linear olefins, and unsaturated terpenes: cyclododecene (Cy12), 1-octene (1nC8), trans-2-octene (2nC8), (R)-(+)-limonene (Lim) and α -pinene (Pin) (Table 3). Steric effects seemed to be important for Cy12 since the reaction with this substrate was slower than with (less bulky) Cy8: 65% and 82% conversion for Cy12 and Cy8, respectively, at 24 h reaction. For the linear C8 olefins 1nC8 and 2nC8, the corresponding epoxides were always the only reaction products. On the basis of the mechanistic points mentioned above, the higher reactivity of 2nC8 in comparison to 1nC8 is likely due to electronic effects, which may offset any steric disadvantage arising from the internal location of the double bond. The double bond of 2nC8 possesses greater electronic density than that of 1nC8, and thus the former may be more susceptible to electrophilic attack by an oxidizing species, leading to a faster epoxidation reaction. This hypothesis is supported by the catalytic results for Lim as substrate, which possesses terminal and endocyclic double bonds. The main reaction product was 1,2-limonene oxide (85% selectivity at 68% conversion), and limonene diepoxide was formed with 8% selectivity. These results demonstrate a high regioselectivity in favor of the epoxidation of the

endocyclic double bond relative to the (less hindered, but electron poorer) exocyclic one. The reaction of Pin with TBHP in the presence of **1** gave α -pinene oxide with 67% selectivity at 50% conversion. A complex mixture of reaction products was obtained, although these results are fairly good considering the high reactivity of α -pinene oxide.

Compound 1 was further explored as a catalyst for the oxidation of alcohols, namely cyclooctanol, cyclohexanol, 1-cyclohexylethanol, sec-phenethyl alcohol and benzyl alcohol, at 55 °C (Table 3). Apart from benzyl alcohol, the corresponding aldehyde/ketone products were formed in high selectivity (94-100% selectivity at 45–68% conversion, 24 h reaction). No reaction occurred without TBHP, indicating that the dehydrogenation of the alcohols is an oxidative process. To the best of our knowledge, this is the first report of oxydehydrogenation activity of an organotin metalate for the reaction of alcohols with a hydroperoxide oxidant to give carbonyl products. The reaction of benzyl alcohol in the presence of 1 led to benzaldehyde and benzoic acid with 24% and 72% selectivity, respectively, at 78% conversion, indicating the ability of 1 for the cascade reaction of alcohol-to-aldehyde-to-carboxylic acid.

For 1, the reaction mixtures were always biphasic solidliquid. The solid catalyst was separated from the Cy8 reaction mixture by filtration (at 24 h reaction) and used in a second run (after washing with *n*-pentane and drying at room temperature overnight). The recovered solid led to similar catalytic results to the fresh catalyst, suggesting that 1 is fairly stable (Figure 6, Table 3). On the other hand, a hot filtration test (details in the experimental section) for 1 led to similar catalytic results to those for a normal catalytic test (without catalyst filtration), indicating that the reaction occurred in homogeneous phase (Figure 6). The elemental composition of the solid phase recovered in the hot filtration test was semi-quantitatively analyzed by energy dispersive X-ray spectroscopy (EDS), and



Figure 5. Kinetic profiles of the epoxidation of Cy8 with TBHP in the presence of 1, without a cosolvent (\bigcirc), or using 1,2-dichloroethane (+), *n*-hexane (\square) or CH₃CN (×) as cosolvent, at 55 °C.

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Figure 6. Hot filtration test carried out for 1 in the epoxidation of Cy8 with TBHP, at 55 °C (×), and comparison with the reaction of Cy8 under normal conditions without filtration of the solid catalyst (first run (\bigcirc); second run (\bigcirc)). CyO selectivity was always 100%.

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the results were compared with those obtained for assynthesized **1**. In both cases a Sn/V molar ratio of ca. 0.9 was obtained, and the elemental spectra were similar (Figure S5 in the Supporting Information). These results suggest that the elemental composition of **1** (i.e. Sn/V = 1) was retained for the dissolved metal species. The filtrate obtained from the hot filtration test of **1** at 40 min reaction was analyzed by ICP-OES, which indicated that ca. 24 mol% of the initial amount of **1** had dissolved. This corresponds to a catalyst solubility of ca. 4.5 mM, and an initial turnover frequency (TOF) of ca. 252 molmol⁻¹_Vh⁻¹, which is more than double that reported previously for the trimethyltin vanadate [Me₃SnVO₃] (82 mol mol⁻¹_Vh⁻¹),^[15] and at least an order of magnitude greater than those for [(*n*Bu₃Sn)₂MO₄] (M=Mo, W)^[10b] and [((Me)₂(menthyl) Sn)₂MoO₄(H₂O)_{3.5}],^[26] tested as catalysts in the same reaction.

Conclusions

The successful synthesis and structural elucidation of the coordination polymer [Et₃SnVO₃] (1) has provided an excellent opportunity to examine the structure-directing role of the tinbonded groups by comparison with the known polymer [Me₃SnVO₃]. In both compounds metavanadate subunits are linked by R_3Sn^+ cations to form 3D network structures. However, while in [Me₃SnVO₃] the metavanadate subunit consists of infinite chains of corner-sharing {VO₄} tetrahedra, in **1** the subunit is the cyclic tetranuclear anion $[V_4O_{12}]^{4-}$. Compound 1 is the first example of an organotin metalate with the sodalite topology. Interesting results were obtained when using 1 as a catalyst in oxidative transformations with *tert*-butyl hydroperoxide as oxidant. Under the reaction conditions used, 1 acts a solid reservoir for soluble, catalytically active species, which promote high selectivities in the epoxidation of olefins and the oxidation of alcohols to give carbonyl products. The intrinsic activity (TOF) for the reaction of the model substrate cis-cyclooctene compares favorably with values determined for other organotin metalates. We conclude that 1 is a promising catalyst for oxidative transformations and that other interesting catalytic materials may be found by expanding the family of hybrid organotin vanadates, which to date is limited to only a handful of compounds.

Experimental Section

Materials and Methods

Ammonium metavanadate (Fluka), triethyltin chloride (Alfa Aesar), acetone (99.5%, Fluka), dimethylformamide (99%), *n*-pentane (99%), 1,2-dichloroethane (99%), *n*-hexane (99%), diethyl ether (99.8%), acetonitrile (99.9%) and 5–6 M TBHP in decane were acquired from Sigma-Aldrich unless otherwise indicated, and used as received.

Microanalyses for C, H and N were carried out with a Truspec Micro CHNS 630-200-200 elemental analyzer. Routine X-ray powder diffraction data were collected on an X'Pert MPD Phillips diffractometer (Cu-K α X-radiation, λ = 1.54060 Å) fitted with a curved

graphite monochromator and a flat plate sample holder, in a Bragg-Brentano para-focusing optics configuration (40 kV, 50 mA). Samples were step-scanned in the range from 3.5 to $70^{\circ} 2\theta$ with steps of 0.02° and a counting time of 25 s per step. Thermogravimetric analyses were performed under air using a Shimadzu TGA-50 system with a heating rate of 5° Cmin⁻¹. SEM images were collected using a Hitachi SU-70 microscope operating at 15 kV. Samples were prepared by deposition on aluminum sample holders followed by carbon coating using an Emitech K 950 carbon evaporator. EDS data were collected using the same electron microscope while employing a Bruker Quantax 400 microanalysis system.

FT-IR spectra were collected using KBr (Aldrich 99%, FT-IR grade) pellets on a Mattson-7000 infrared spectrophotometer. FT-Raman spectra were recorded on a Bruker RFS 100 spectrometer with a Nd:YAG coherent laser ($\lambda = 1064$ nm). ¹³C, ⁵¹V and ¹¹⁹Sn solid state NMR spectra were recorded at 100.62, 105.24 and 149.21 MHz, respectively, on a Bruker Avance 400 spectrometer (9.4 T). ¹H-¹³C cross-polarization (CP) MAS NMR spectra were acquired with a spinning rate of 7 kHz, 4.5 µs ¹H 90° pulses, 2 ms contact time and 4 s recycle delays. ⁵¹V MAS NMR spectra were recorded with a spinning rate of 14 kHz, short 0.6 µs (equivalent to 10°) pulses and 5 s recycle delays. ¹¹⁹Sn CP MAS NMR spectra were recorded with a spinning rate of 15 kHz, 3.5 µs ¹H 90° pulses, a contact time of 3 ms and 4 s recycle delays. Chemical shifts are quoted in parts per million (ppm) from SiMe₄ (¹³C), VOCl₃ (⁵¹V) and SnMe₄ (¹¹⁹Sn).

Synthesis of [Et₃SnVO₃] (1)

NH₄VO₃ (0.58 g, 5 mmol) was dissolved in water (40 mL) by stirring and heating the suspension to 60°C for 15 min. A solution of Et₃SnBr (1.43 g, 5 mmol) in acetone (5 mL) was added dropwise to the stirred solution of NH₄VO₃, resulting in the immediate formation of a precipitate. After stirring the mixture for a further 30 min, the solid product was filtered, washed thoroughly with water and dried overnight at 100°C to give compound 1 (1.50 g, 99%) as a pale yellow powder. Anal. Calcd for C₆H₁₅O₃SnV (304.83): C, 23.64; H, 4.96 %. Found: C, 23.76; H, 5.04. FT-IR (KBr, cm⁻¹): ν = 2965 (m), 2946 (m), 2918 (m), 2868 (m), 2821 (w), 2732 (w), 1455 (m), 1419 (w), 1377 (w), 1234 (w), 1187 (w), 1020 (w), 963 (w), 913 (sh), 875 (sh), 807 (vs), 672 (s), 523 (m), 492 (sh), 365 (w). Raman (cm⁻¹): $\nu = 2944$ (m), 2915 (vs), 2870 (m), 2819 (vw), 2733 (vw), 1457 (w), 1420 (w), 1378 (w), 1192 (m), 953 (vs), 918 (m), 863 (w), 566 (w), 523 (w), 486 (s), 444 (m), 367 (w), 251 (m). ¹³C CP MAS NMR: $\delta = 12.6$ (CH₂CH₃), 10.5 (CH₂CH₃) ppm. ¹¹⁹Sn CP MAS NMR: $\delta =$ 74.3 ppm. ⁵¹V MAS NMR: $\delta = -666.3$ ppm.

Single-Crystal X-ray Diffraction Studies

Single crystals of [Et₃SnVO₃] (1) were manually harvested from the crystallization vial and immersed in highly viscous FOMBLIN Y perfluoropolyether vacuum oil (LVAC 140/13, Sigma-Aldrich) to avoid degradation caused by evaporation of the solvent.^[28] Crystals were mounted on Hampton Research CryoLoops with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. X-ray diffraction data were collected at 180(2) K on a Bruker D8 QUEST equipped with a Mo-K α (λ =0.71073 Å) sealed-tube X-ray source, a multilayer TRIUMPH X-ray mirror, a PHOTON 100 CMOS detector, and an Oxford Instruments Cryostream 700 + Series cooler.

Diffraction images were processed using the software package SAINT+,^[29] and data were corrected for absorption by the multiscan semi-empirical method implemented in SADABS.^[30] The structure was solved using the algorithm implemented in SHELXT- 2014,^[31] which allowed the immediate location of almost all of the heaviest atoms composing the molecular unit. The remaining missing and misplaced non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on F^2 using the latest SHELXL from the 2014 release.^[32] All structural refinements were performed using the graphical interface ShelXle.^[33]

Although the inorganic backbone of 1 could be unequivocally located and refined anisotropically, the three crystallographically independent ethyl groups bound to tin atoms were found to be considerably affected by thermal disorder. Each moiety was found to be, at least, disordered over two crystallographic locations. The final structural model contemplated the existence of two sets of locations for the three independent moieties which were refined with complementary rates of occupancy that, ultimately, refined to 83(2) and 17(2) % (please see Figure 2 for additional details). These moieties were refined with the geometry heavily restrained to guarantee chemical reasonableness. Hydrogen atoms bound to carbon were placed at their idealized positions using appropriate HFIX instructions in SHELXL: 23 for the -CH2- moieties and 33 for the terminal methyl groups. These hydrogen atoms were included in subsequent refinement cycles with isotropic thermal displacement parameters (U_{iso}) fixed at 1.2 or $1.5 \times U_{eq}$ of the parent atoms, respectively. The final structural model contains approximately 2564 Å³ of solvent-accessible volume as revealed by PLATON.^[34] These voids contain a considerable smeared-out electron density that prevented a proper modelling of the potential solvent contained therein. The last difference Fourier map synthesis showed the highest peak (2.115 eÅ⁻³) and the deepest hole $(-0.477 \text{ e}\text{\AA}^{-3})$ located at 0.02 and 0.96 Å from Sn1 and H4B, respectively.

Structural drawings were created using Crystal Impact Diamond.^[35] CCDC-1828416 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data request/cif.

Synchrotron Powder X-ray Diffraction Studies

High-resolution powder synchrotron X-ray diffraction data for [Et₃SnVO₃] (1) were collected at low temperature (110 K; cooling device from Oxford Instruments) on the powder diffractometer instrument assembled at the Swiss-Norwegian beam line BM01b at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The beam line receives X-rays from the synchrotron source, operating with an average energy of 6 GeV and a typical beam current of 200 mA, from a bending magnet device. The high signal-to-noise ratio of the data is due to the high brilliance of the synchrotron beam in combination with a Si (111) crystal multi-analyzer.

The monochromatic wavelength was fixed at 0.504884(8) Å and calibrated against the Si standard NIST 640c [certified cell parameter a = 5.4311946(92) Å]. Hard X-rays were selected for data collection to significantly reduce radiation damage. Even at low temperature the high brilliance of the synchrotron source led to visible damage on the samples. To minimize such effects consecutive data collections were performed on fresh portions of the samples by translating the capillaries by *ca.* 1.3 mm.

A finely powdered sample of **1** was placed inside a Hilgenberg borosilicate glass capillary with a diameter of *ca.* 0.6 mm, which was spun during data collection to improve powder averaging over the individual crystallites, ultimately removing textural effects (such as preferred orientation). Data were collected in continuous mode with accumulation times increasing with the scattering angle. The

counts of six detectors (covering roughly $5.5^{\circ} 2\theta$) were rebinned and normalized to give the equivalent step scans (0.002°) suitable for further structural analyses.

The collected high-resolution powder XRD pattern was indexed using the LSI-Index algorithm implemented in TOPAS-Academic V5,^[36] and a whole-powder-pattern Pawley fit unequivocally confirmed once again the cubic *F*-43c space group as being the most suitable. The crystal structure was determined in TOPAS-Academic V5^[36a] by using a simulated annealing approach. Rietveld structural refinements^[37] were performed in the same programme using a Chebychev polynomial throughout the entire angular range to model the background contribution, and using the atomic coordinates as provided from the single-crystal XRD studies performed (see previous section). Atomic coordinates were allowed to refine against the powder data with virtually the same structure being derived from both models. A modified Thompson-Cox-Hastings pseudo-Voigt (TCHZ) profile function was selected to generate the line shapes of the simulated diffraction peaks.^[38]

Catalysis

The catalytic reactions were carried out at 55°C under air atmosphere, using batch reactors (5 mL capacity) equipped with a magnetic stirrer and a valve for sampling. The reactor was loaded with the catalyst [Et₃SnVO₃] (1) (28 µmol), substrate (3.6 mmol) and ca. 5.5 mmol tert-butyl hydroperoxide (ca. 5.5 M in decane). The reactions were typically carried out without additional solvent (other than the decane present in the TBHP solution). For the substrate Cy8, the reaction was also carried out using a cosolvent (1 mL), namely 1,2-dichloroethane, n-hexane or acetonitrile. Samples were withdrawn periodically and analyzed using a Varian 3800 GC equipped with a capillary column (DB-5, 30 m×0.25 mm for the reactions of the olefins, and CP WAX 52CB, 30 m×0.53 mm for the reactions of the alcohols) and a FID detector. The products were quantified using calibration curves with *n*-nonane or undecane as internal standard (added after the reaction). The reaction products were identified by GC-MS [Trace GC 2000 Series (Thermo Quest CE Instruments) - DSQ II (Thermo Scientific), equipped with a capillary DB-1 column (30 m \times 0.25 mm; 0.25 $\mu m)$ and using He as carrier gas]. A hot filtration test was carried out for 1 as follows: the reaction mixture was filtered at 40 min reaction and 55 °C, using a 0.2 µm PTFE membrane, and subsequently the filtrate was left to react further at 55 °C.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: vanadates \cdot tin \cdot sodalite topology \cdot epoxidation \cdot oxidative dehydrogenation

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Let there be sodalite: The coordination polymer $[Et_3SnVO_3]$ (1) possesses a three-dimensional network structure with the sodalite topology, formed by tetravanadate polyanions, $[V_4O_{12}]^{4-}$, that are linked by Et_3Sn^+ spacers. The catalytic versatility of 1 was demonstrated by applying it for the epoxidation of olefins, the oxidative dehydrogenation of alcohols, and the oxidation of benzyl alcohol.



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An Organotin Vanadate with Sodalite Topology and Catalytic Versatility in Oxidative Transformations

