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Hybrid Organic–Inorganic Assemblies Based on Molybdates and Dimethyltin Linkers

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Reaction of $(CH_3)_2SnCl_2$ with Na_2MoO_4 in an aqueous medium results in three different compounds depending on the pH: $[\{(CH_3)_2Sn\}(MoO_4)]$ (**1**), $[\{(CH_3)_2Sn\}_4O_2(MoO_4)_2]$ (**2**), and $[\{(CH_3)_2Sn\}\{Mo_2O_7(H_2O)_2\}]\cdot H_2O$ (**3**). All three species have been characterized in the solid state by means of elemental analysis, infrared spectroscopy, thermogravimetry, and single-crystal X-ray diffraction. Compounds **1**–**3** all show hybrid organic–inorganic extended lattices based on molybdate anions linked by $(CH_3)_2Sn^{2+}$ moieties, and the coordination numbers of the Sn(IV) centers range from 5 to 7. Compound **1** crystallizes in the orthorhombic space group *Pnma* with cell parameters $a = 13.2035(4)$ Å, $b = 7.2634(2)$ Å, $c = 7.1458(2)$ Å, and $Z = 4$. **1** exhibits a complex, 3-dimensional network structure constructed of corner-shared, tetrahedral orthomolybdate oxoanions and distorted octahedral *trans*-$(CH_3)_2SnO_4$ groups. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with cell parameters $a = 8.2330(1)$ Å, $b = 11.4033(2)$ Å, $c = 12.1529(2)$ Å, $\beta = 91.566(1)°$, and $Z = 2$. Its 2-dimensional layered structure contains dimeric tetramethyldistannoxane $[\{(CH_3)_2Sn\}_4O_2]^{2+}$ subunits built up of edge-sharing *cis*-$(CH_3)_2SnO_4$ distorted trigonal bipyramids and connected in the $(1,0,\bar{1})$ plane by tetrahedral orthomolybdate oxoanions, the layers packing along the crystallographic *a* axis with the methyl groups pointing to the interlamellar space. Compound **3** crystallizes in the orthorhombic space group *Pbcm* with cell parameters $a = 6.5594(4)$ Å, $b = 14.2465(11)$ Å, $c = 11.3892(8)$ Å, and $Z = 4$. It shows dimeric $[Mo_2O_8(H_2O)_2]$ units sharing corners to form zigzagging polymeric $\{[Mo_2O_7(H_2O)_2]^{2-}\}_\infty$ polyanions along the [001] direction; these chains are further linked by *trans*-$(CH_3)_2SnO_5$ distorted pentagonal bipyramids to give layers parallel to the (010) plane, the interlamellar space being occupied by hydrogen-bonded hydration water molecules.

Introduction

Polyoxometalates (POMs) constitute a large family of anionic metal−oxygen cluster compounds of enormous compositional, structural, and electronic versatility. These features endow POMs with a multitude of interesting properties and resulting applications in a wide range of fields, including catalysis, materials science, or medicine.[1] To improve the selectivity of POMs to specific targets, there have been increasing efforts worldwide to systematically derivatize POM clusters via their functionalization with organic or organometallic moieties covalently attached to the metal−oxo surface. Monoorganotin(IV) species (e.g., $C_6H_5SnCl_3$) have hydrolytically and oxidatively stable Sn−C bonds, and the size of Sn(IV) is appropriate to substitute addenda metal centers in POM skeletons. These properties make monoorganotin moieties good candidates for the derivatization of POMs, and therefore, their reaction with lacunary heteropolytungstates has been deeply investigated over the past several years, predominantly by the groups of Pope,[2] Knoth,[3] Liu,[4] and Hasenknopf.[5] This work has led to several examples of monomeric or dimeric hybrid POMs

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[1] (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, Germany, 1983. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (c) *Polyoxometalates: From Platonic Solids to Antiretroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, The Netherlands, 1994. (d) Hill, C. L., Ed. *Chem. Rev.* **1998**, *98* (1), special thematic issue. (e) *Polyoxometalate Chemistry: From Topology via self-Assembly to Applications*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, The Netherlands, 2001. (f) *Polyoxometalate Chemistry for Nanocomposite Design*; Pope, M. T., Yamase, T., Eds.; Kluwer: Dordrecht, The Netherlands, 2002. (g) *Polyoxometalate Molecular Science*; Borrás-Almenar, J. J., Coronado, E., Müller, A., Pope, M. T., Eds.; Kluwer: Dordrecht, The Netherlands, 2003. (h) Pope, M. T. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J, Eds.; Elsevier Ltd.: Oxford, U.K., 2004.

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containing tightly bound RSn^{3+} functionalities, which fulfill the essential requirements of being water-soluble and stable at physiological pH for potential pharmaceutical applications.[6] Recently, our group has demonstrated that diorganotin(IV) electrophiles (e.g., *trans*-$(CH_3)_2Sn^{2+}$) can also be used as highly efficient linkers of lacunary polyoxotungstates to construct large discrete clusters with unprecedented architectures, examples ranging from monomeric to dodecameric assemblies.[7]

Now, we have decided to study the interaction of the $(CH_3)_2Sn^{2+}$ electrophile toward other types of POMs, and more specifically toward polyoxomolybdates. Therefore, as the first step we checked the reactivity in the $(CH_3)_2Sn^{2+}$/MoO_4^{2-} system with the pH as the single variable parameter. The interest in combining these building blocks lies in the fact that related organotin−oxometalate coordination polymers have been shown to be efficient and selective heterogeneous catalysts for the epoxidation of olefins and for sulfoxidation processes at room temperature and pressure.[8]

Here we report on the synthesis, crystal structure, and solid-state characterization of three different compounds obtained from the reaction of $(CH_3)_2SnCl_2$ with Na_2MoO_4 in an aqueous medium in different pH ranges: $[\{(CH_3)_2Sn\}(MoO_4)]$ (**1**), $[\{(CH_3)_2Sn\}_4O_2(MoO_4)_2]$ (**2**), and $[\{(CH_3)_2Sn\}\{Mo_2O_7(H_2O)_2\}]\cdot H_2O$ (**3**).

Experimental Section

Materials and Methods. All reagents were used as purchased without further purification. The Sn and Mo elemental analyses were performed by ANALYTIS, Gesellschaft für Laboruntersuchungen mbH, Wesseling bei Köln, Germany, whereas the C and H elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, Germany. Infrared spectra for solid samples were obtained as KBr pellets on a Nicolet Avatar 370 FTIR spectrophotometer. Thermogravimetric analyses were carried out on a TA Instruments SDT Q600 thermobalance with a 100 mL/min flow of nitrogen; the temperature was ramped from 20 to 800 °C at a rate of 5 °C/min.

Synthesis of $[\{(CH_3)_2Sn\}(MoO_4)]$ (1). Compound **1** was obtained as colorless rodlike single crystals suitable for X-ray diffraction in an attempt to synthesize a dimethyltin(IV)-containing phosphomolybdate by the following method: To an aqueous solution (30 mL) of $Na_2MoO_4\cdot 2H_2O$ (0.726 g, 3 mmol) and Na_2HPO_4 (0.071 g, 0.5 mmol) was added solid $(CH_3)_2SnCl_2$ (0.220 g, 1 mmol) under vigorous stirring. After the clear reaction mixture was stirred for 30 min at room temperature, 2.5 mL of aqueous 1 M NH_4Cl was added, and the resulting solution was left to slowly evaporate at room temperature, crystals forming in a few days. Alternatively, compound **1** can be prepared as a white powder by mixing $Na_2MoO_4\cdot 2H_2O$ (0.726 g, 3 mmol) and $(CH_3)_2SnCl_2$ (0.220 g, 1 mmol) in 30 mL of water (mixture A, pH 5.8). Yield: 60% based on Sn. Anal. Calcd (found) for $C_2H_6MoO_4Sn$: C, 7.78 (7.82); H, 1.98 (1.99); Mo, 31.08 (29.3); Sn 38.45 (41.1). IR (cm^{-1}): 1202(w), 1193(w), 940(s), 913(s), 869(vs), 756(vs), 596(w), 526(w).

Synthesis of $[\{(CH_3)_2Sn\}_4O_2(MoO_4)_2]$ (2). To mixture A was added aqueous 6 M NaOH until compound **1** dissolved (final pH 7.2). The reaction mixture was stirred for 30 min at room temperature, and after approximately 20 min a small amount of a white solid impurity appeared which was filtered off. After addition of 2.5 mL of aqueous 1 M NH_4Cl, the resulting solution was left to slowly evaporate at room temperature. Colorless blocklike single crystals suitable for X-ray diffraction were obtained in a few days. Yield: 30% based on Sn. Anal. Calcd (found) for $C_8H_{24}Mo_2O_{10}Sn_4$: C, 10.15 (10.15); H, 2.55 (2.54); Mo, 20.26 (18.0); Sn 50.14 (49.7). IR (cm^{-1}): 1205(w), 940(m), 906(m), 900(m), 863(m), 848(m), 787(s), 772(s), 748(s), 724(s), 565(vs), 556(vs).

Synthesis of $[\{(CH_3)_2Sn\}\{Mo_2O_7(H_2O)_2\}]\cdot H_2O$ (3). To mixture A was added aqueous 6 M HCl until compound **1** dissolved (final pH 1.9). After being stirred for 30 min at room temperature, the resulting solution was left to slowly evaporate at room temperature, and colorless tablet-like single crystals suitable for X-ray diffraction were obtained in a few days. Alternatively, compound **3** can be obtained as a white powder by heating the above solution at 100 °C for 30 min instead of stirring it at room temperature. Yield: 20% based on Sn. Anal. Calcd (found) for $C_2H_{12}Mo_2O_{10}Sn$: C, 4.74 (4.64); H, 2.39 (2.45); Mo, 37.87 (35.7); Sn 23.43 (23.7). IR (cm^{-1}): 1192(w), 933(m), 899(s), 797(m), 724(m), 548(s), 434(w).

X-ray Crystallography. Single crystals of compounds **1**−**3** were mounted in Hampton cryoloops using light oil for indexing and intensity data collection at 173 K (**1** and **3**) or 297 K (**2**) on a Bruker X8 APEX II CCD single-crystal diffractometer with κ geometry and Mo Kα radiation ($\lambda = 0.71073$ Å). Data integration was performed using the SAINT software. Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program.[9] Direct methods were used to solve the structure and to locate the heavy atoms (SHELXS97).[10] The remaining atoms were found from successive Fourier syntheses (SHELXL97).[10] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the methyl groups were placed in calculated positions using a riding model standard

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(2) (a) Zonnevijlle, F.; Pope, M. T. *J. Am. Chem. Soc.* **1979**, *101*, 2211. (b) Xin, F.; Pope, M. T. *Organometallics* **1994**, *13*, 4881. (c) Xin, F.; Pope, M. T. *Inorg. Chem.* **1996**, *35*, 5693. (d) Xin, F.; Pope, M. T.; Long, G. J.; Russo, U. *Inorg. Chem.* **1996**, *35*, 1207. (e) Sazani, G.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **2000**, *39*, 939. (f) Sazani, G.; Pope, M. T. *Dalton Trans.* **2004**, 1989.

(3) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759. (b) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 2211. (c) Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 818. (d) Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1985**, *4*, 32.

(4) (a) Yang, Q. H.; Dai, H. C.; Liu, J. F. *Transition Met. Chem. (Dordrecht, Neth.)* **1998**, *23*, 93. (b) Wang, X. H.; Dai, H. C.; Liu, J. F. *Polyhedron* **1999**, *18*, 2293. (c) Wang, X. H.; Dai, H. C.; Liu, J. F. *Transition Met. Chem. (Dordrecht, Neth.)* **1999**, *24*, 600. (d) Wang, X. H.; Liu, J. F. *J. Coord. Chem.* **2000**, *51*, 73. (e) Wang, X. H.; Liu, J. T.; Zhang, R. C.; Li, B.; Liu, J. F. *Main Group Met. Chem.* **2002**, *25*, 535.

(5) (a) Bareyt, S.; Piligkos, S.; Hasenknopf, B.; Gouzerh, P.; Lacôte, E.; Thorimbert, S.; Malacria, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3404. (b) Bareyt, S.; Piligkos, S.; Hasenknopf, B.; Gouzerh, P.; Lacôte, E.; Thorimbert, S.; Malacria, M. *J. Am. Chem. Soc.* **2005**, *127*, 6788.

(6) (a) Rhule, J. T.; Hill, C. L.; Judd, D. A. *Chem. Rev.* **1998**, *98*, 327. (b) Sarafianos, S. G.; Kortz, U.; Pope, M. T.; Modak, M. J. *Biochem. J.* **1996**, *319*, 619.

(7) (a) Hussain, F.; Reicke, M.; Kortz, U. *Eur. J. Inorg. Chem.* **2004**, 2733. (b) Hussain, F.; Kortz, U. *Chem. Commun.* **2005**, 1191. (c) Kortz, U.; Hussain, F.; Reicke, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3773. (d) Hussain, F.; Kortz, U.; Keita, B.; Nadjo, L.; Pope, M. T. *Inorg. Chem.* **2006**, *45*, 761.

(8) (a) Abrantes, M.; Valente, A.; Pillinger, M.; Gonçalves, I. S.; Rocha, J.; Romão, C. C. *J. Catal.* **2002**, *209*, 237. (b) Abrantes, M.; Valente, A.; Pillinger, M.; Gonçalves, I. S.; Rocha, J.; Romão, C. C. *Chem.—Eur. J.* **2003**, *9*, 2685. (c) Abrantes, M.; Valente, A.; Gonçalves, I. S.; Pillinger, M.; Romão, C. C. *J. Mol. Catal. A* **2005**, *238*, 51.

(9) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 1996.

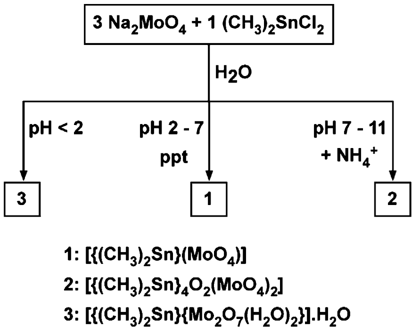
(10) Sheldrick, G. M. *SHELX-97 Program System for Crystal Structure Determination and Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystallographic Data for Compounds **1**−**3**

	1	2	3
empirical formula	$C_2H_6MoO_4Sn$	$C_8H_{24}Mo_2O_{10}Sn_4$	$C_2H_{12}Mo_2O_{10}Sn$
fw	308.7	947.0	506.7
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*Pnma*	$P2_1/n$	*Pbcm*
a (Å)	13.2035(4)	8.2330(1)	6.5594(4)
b (Å)	7.2634(2)	11.4033(2)	14.2465(11)
c (Å)	7.1458(2)	12.1529(2)	11.3892(8)
β (deg)		91.566(1)	
V (Å^3)	685.30(3)	1140.53(3)	1064.30(13)
D_{calcd} (g cm^{-3})	2.992	2.757	3.162
Z	4	2	4
μ (mm^{-1})	5.409	5.414	4.685
no. of collected reflns	22643	69940	20737
no. of unique reflns (R_{int})	3456 (0.067)	8211 (0.045)	1520 (0.095)
no. of obsd reflns ($I > 2\sigma I$)	2519	6341	1241
no. of params	46	110	77
$R(F)^a$ (obsd reflns)	0.041	0.026	0.029
$R_w(F^2)^a$ (all reflns)	0.104	0.069	0.069
GOF	1.002	1.000	1.029

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Scheme 1. Synthetic Procedure for Compounds **1**−**3**



SHELXL parameters. Crystallographic data for compounds **1**−**3** are summarized in Table 1.

Results and Discussion

Synthesis. To investigate the reactivity of the $(CH_3)_2Sn^{2+}$ electrophile toward polyoxomolybdates in an aqueous medium, Na_2MoO_4 was reacted with $(CH_3)_2SnCl_2$ in a 3:1 ratio at different pH values ranging from 0 to 12 (Scheme 1). The reactions were carried out either at room temperature or at around 70 °C, giving the same final product in all cases. As previously reported by Rochow et al.,[11] when Na_2MoO_4 is treated with $(CH_3)_2SnCl_2$, compound **1** is formed immediately as a precipitate, the pH of the reaction mixture being approximately 6. This precipitate can be obtained when the reaction is performed under pH conditions ranging from neutral to highly acidic (pH ≈ 2). However, if the reaction is carried out in the presence of Na_2HPO_4, the precipitation of compound **1** is avoided and single crystals suitable for X-ray diffraction studies can be obtained from the slow evaporation of the resulting solution. Although not present in the composition of the final compound, we observed that the crystallization was improved by the addition of NH_4^+ or K^+ cations to this solution, but in contrast the presence of Cs^+ ions led to a mixture of crystals of compound **1** and $Cs_5[PMo_8O_{28}(OH)_2]\cdot 2H_2O$.[12] On the other hand, compound **1** redissolves when the pH of the reaction mixture is increased to above 7. The crystals isolated from this solution by slow evaporation correspond to compound **2**. This compound can be synthesized in good yield at pH values ranging from neutral to highly basic (~11.5). We observed also in this case that the crystallization was improved by addition of NH_4^+ cations, the presence of K^+ or Cs^+ ions giving mixtures with a small amount of powder corresponding to an unidentified compound. Similarly, compound **1** also redissolves in a highly acidic aqueous medium when the pH is decreased to below 2, leading to the formation of crystals of compound **3** if no extra alkaline cations are added to the reaction medium. In contrast, if K^+, NH_4^+, or Cs^+ ions are added, the corresponding salts of the well-known $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ isopolyoxomolybdate[13] are isolated on the basis of infrared spectroscopy.

Infrared Spectroscopy and Thermal Analysis. The infrared spectra (Figure S1 in the Supporting Information) unambiguously indicate the presence of the $(CH_3)_2Sn^{2+}$ moiety in all three compounds, although no analogies could be found in the region below 1000 cm^{-1} (corresponding to the metal−oxygen stretching and bending modes). The infrared spectra show single or double peaks of weak intensity around 1200 cm^{-1} (**1**, 1202 and 1193 cm^{-1}; **2**, 1205 cm^{-1}; **3**, 1192 cm^{-1}), which are characteristic of methyltin(IV) derivatives and can be assigned to the symmetrical bending vibration of the methyl groups, $\delta_s(CH_3)$.[14]

Thermal analysis for compounds **1** and **2** with a N_2 atmosphere shows similar trends (Figure S2 in the Supporting Information). Both species are anhydrous and thermally stable up to relatively high temperatures (245 and 315 °C for **1** and **2**, respectively), after which they undergo a single endothermic decomposition process which involves not only loss of the methyl groups, but also of some oxygens [**1**, mass loss calculated for $C_2H_6O_2$ (found) 20.10% (19.93%); **2**, mass loss calculated for $C_8H_{24}O_6$ (found) 22.84% (23.39%)]. The decomposition ends at 360 °C for both compounds, but just above this temperature an increase of mass takes place, which leads to stable phases at 625 °C [**1**, calculated for $SnMoO_3$ (found) 14.92% (15.83%)] and 605 °C [**2**, calculated for $Sn_4Mo_2O_6$ (found) 19.46% (21.22%)]. In the case of compound **3** (Figure S3 in the Supporting Information), thermal analysis with a N_2 atmosphere shows that it is stable up to 40 °C, after which it undergoes a single endothermic dehydration process involving the release of both the hydration water molecules and those coordinated to the molybdenum atoms [mass loss calculated for $3H_2O$ (found) 10.66% (10.76%)]. The dehydration step finishes at 155 °C, leading to the corresponding anhydrous phase, $C_2H_6Mo_2O_7Sn$, which is thermally stable up to 250 °C. Above this temperature,

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(11) Rochow, E. G.; Seyferth, D.; Smith, A. C., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 3099.

(12) Dumas, E.; Sevov, S. C. *Inorg. Chem.* **2002**, *41*, 144.

(13) (a) Krebs, B.; Paulat-Böschen, I. *Acta Crystallogr.* **1982**, *B38*, 1710. (b) Krebs, B.; Stiller, S.; Tytko, K. H.; Mehmke, J. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 883.

(14) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1997.

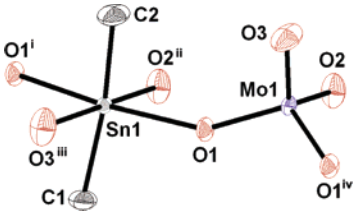

Figure 1. ORTEP view of the asymmetric unit of compound **1** together with the labeling scheme (50% probability displacement ellipsoids; hydrogen atoms have been omitted for clarity). Symmetry codes: (i) x, $1/2 - y$, z; (ii) $1 - x$, $1/2 + y$, $1 - z$; (iii) $1/2 - x$, $-y$, $-1/2 + z$; (iv) x, $-1/2 - y$, z.

decomposition of the compound takes place in a single mass loss originating from at least two different, highly overlapping endothermic processes. As in compounds **1** and **2**, this decomposition step involves loss not only of the methyl groups, but also of one oxygen atom per formula [mass loss calculated for C_2H_6O (found) 9.10% (8.77%)], in such a way that the final thermogravimetric residue is formed above 340 °C [calculated for $SnMo_2O_6$ (found) 80.24% (80.11%)].

Crystal Structure of Compound 1. In 1984, Sasaki et al. reported the room-temperature single-crystal X-ray structure determination of compound **1** in the tetragonal space group $P4_2/mbc$, as determined by Weissenberg techniques.[15] However, our studies show that at room and also at low temperature (293 and 173 K, respectively) compound **1** can be best described as crystallizing in the orthorhombic space group *Pnma* with one Mo atom and one Sn atom in the asymmetric unit (Figure 1). The crystal structure shows a complex 3-dimensional network of orthomolybdate oxoanions linked together by *trans*-$(CH_3)_2Sn^{2+}$ moieties. The Mo center is tetrahedrally coordinated by four oxygen atoms, the bond lengths and angles being not unusual for an orthomolybdate. On the other hand, the coordination geometry around the Sn atom is distorted octahedral $(CH_3)_2SnO_4$, with the two methyl groups occupying relative *trans* positions. The Sn−C bond lengths are short (2.088(6) and 2.097(5) Å), and the C−Sn−C angle (167.0(2)°) deviates significantly from linearity. These geometric parameters are in agreement with those observed for the octahedrally coordinated Sn atoms present in our previously reported dimethyltin-containing polyoxotungstates.[7] All four oxygen atoms occupying equatorial positions belong to orthomolybdate oxoanions, but the Sn−O bonding is not regular and can be described as one short bond (2.129(4) Å), two long bonds (2.209 Å), and one very long bond (2.394(4) Å). Moreover, the Sn1−O1−Mo1 bond angle is substantially smaller (148.4(1)°) than those angles involving O2 and O3, which are nearly linear (179.6(2)° and 176.3(2)°, respectively). Selected bond lengths and angles for the Sn center are given in Table 2.

The 3-dimensional network structure of compound **1** can be described as ladder-like double chains running parallel to the [010] direction. They are formed by linearly fused eight-membered rings of alternating corner-shared MoO_4 tetrahedra and $(CH_3)_2SnO_4$ octahedra, the bridging oxygen atoms being O1 and O2. These double chains are stacked along the crystallographic *c* axis, and each of them is connected to four neighboring double chains (belonging to adjacent stacks) through very long Mo1−O3−Sn1 bridges. This arrangement leads to an intricate 3-dimensional lattice in which the methyl groups point to the center of the space delimited by four interconnected double chains (Figure 2).

Crystal Structure of Compound 2. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with one Mo atom and two Sn atoms in the asymmetric unit (Figure 3). The crystal structure shows a 2-dimensional arrangement of dimeric tetramethyldistannoxane $[\{(CH_3)_2Sn\}_4O_2]^{2+}$ subunits connected through orthomolybdate oxoanions. As in compound **1**, the Mo center is located in a tetrahedral MoO_4 coordination environment and the bond lengths and angles are not unusual. On the other hand, the $[\{(CH_3)_2Sn\}_4O_2]^{2+}$ subunit is composed of a centrosymmetric, rhombic Sn_2O_2 cyclic core, with each bridging oxo group acting in a tridentate fashion by coordinating an exocyclic Sn atom. In addition, the molybdate oxoanions act both as bidentate μ^2-O bridges between endo- and exocyclic Sn centers (Sn2 and Sn1, respectively) and as monodentate ligands to the latter via the O2 and O3 atoms, respectively. Both of the crystallographically independent Sn centers are pentacoordinated and exhibit highly distorted coordination geometries which are best described as trigonal-bipyramidal. The equatorial plane is defined by the μ^3-O1 oxo group and the methyl groups, which therefore occupy relative *cis* positions. In both cases, the bridging O2 atom is located in one of the axial positions, whereas the other one is occupied by the monodentate molybdate and specifically the μ^3-O1^i group for Sn1 and Sn2, respectively. All the Sn−C (Sn1, 2.097(2) and 2.102(3) Å; Sn2, 2.101(2) and 2.102(2) Å) and Sn−O (Sn1, 2.028(1) and 2.101(2) Å; Sn2, 2.035(2) and 2.108(1) Å) bond lengths are short with the exception of those involving the O2 atom (2.385(2) and 2.28(2) Å for Sn1 and Sn2, respectively). On the other hand, the distortion from the ideal trigonal-bipyramidal geometry is reflected in both the axial O−Sn−O (Sn1, 159.35(6)°; Sn2, 150.14(6)°) and the equatorial C−Sn−C (Sn1, 145.7(1)°; Sn2, 132.6(1)°) bond angles (Table 2).

This type of tetrameric, ladder-like cluster formed by edge-shared *cis*-$(CH_3)_2SnO_3$ trigonal bipyramids with an almost planar tin−oxo skeleton is a common structural motif in diorganotin(IV) chemistry. A large number of these compounds with different anions (e.g., halide, hydroxide, carboxylate) acting as terminal ligands or μ^2-bridges have been structurally characterized previously.[16] However, to our knowledge compound **2** constitutes the first example of a

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(15) Sasaki, Y.; Imoto, H.; Nagano, O. *Bull. Chem. Soc. Jpn*. **1984**, *57*. 1417.

(16) See for example: (a) Puff, H.; Friedrichs, E.; Visel, F. *Z. Anorg. Allg. Chem*. **1981**, *477*, 50. (b) Vatsa, C.; Jain, V. K.; Das, T. K.; Tiekink, E. R. T. *J. Organomet. Chem*. **1991**, *418*, 329. (c) Schoop, T.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *Organometallics* **1993**, *12*, 571. (d) Tiekink, E. R. T.; Gielen, M.; Bouhdid, A.; Biesemans, M.; Willem, R. *J. Organomet. Chem*. **1995**, *494*, 247. (e) Beckmann, J.; Jurkschat, K.; Kaltenbrunner, U.; Rabe, S.; Schürmann, M. *Organometallics* **2000**, *19*, 4887. (f) Beckmann, J.; Henn, M.; Jurkschat, K.; Schürmann, M. *Organometallics* **2002**, *21*, 192. (g) Ma, C.; Sun, J. *Dalton Trans*. **2004**, 1785. (h) Ma, C.; Han, Y.; Zhang, R. *J. Organomet. Chem*. **2004**, *689*, 1675. (i) Zheng, G.-L.; Ma, J.-F.; Yang, J.; Li, Y.-Y.; Hao, X.-R. *Chem.*−*Eur. J*. **2004**, *10*, 3761. (j) Benetollo, F.; Gioia Lobia, G.; Mancini, M.; Pellei, M.; Santini, C. *J. Organomet. Chem*. **2005**, *690*, 1994.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Sn Atoms in Compounds **1**−**3**[a]

		2					
1		Sn1		Sn2		**3**	
Sn1−C1	2.097(5)	Sn1−C1	2.102(3)	Sn2−C3	2.102(2)	Sn1−C1	2.082(7)
Sn1−C2	2.088(6)	Sn1−C2	2.097(2)	Sn2−C4	2.101(2)	Sn1−C2	2.100(7)
Sn1−O1	2.209(2)	Sn1−O1	2.028(1)	Sn2−O1	2.035(2)	Sn1−O1	2.236(5)
Sn1−O1^{i}	2.209(2)	Sn1−O2	2.385(2)	Sn2−O1^{i}	2.108(1)	Sn1−O3^{i}	2.426(3)
Sn1−O2^{ii}	2.129(4)	Sn1−O3	2.101(2)	Sn2−O2	2.282(2)	Sn1−O3^{ii}	2.426(3)
Sn−O3^{iii}	2.394(4)					Sn1−O4^{iii}	2.243(2)
						Sn1−O4^{iv}	2.243(2)
C1−Sn1−C2	167.0(2)	C1−Sn1−C2	145.7(1)	C3−Sn1−C4	136.2(1)	C1−Sn1−C2	168.6(3)

[a] Symmetry codes: (**1**) (i) x, $1/2 - y$, z; (ii) $1 - x$, $1/2 + y$, $1 - z$; (iii) $1/2 - x$, $-y$, $-1/2 + z$; (**2**) (i) $1 - x$, $2 - y$, $2 - z$; (**3**) (i) $1 + x$, y, $3/2 - z$; (ii) $1 + x$, y, z; (iii) $1 - x$, $1 - y$, $1 - z$; (iv) $1 - x$, $1 - y$, $1/2 + z$.

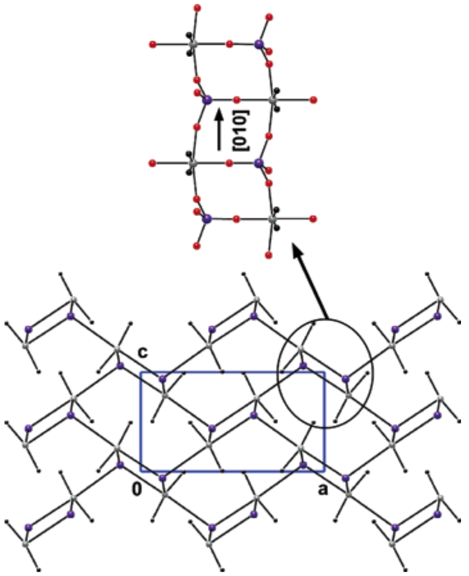

Figure 2. Top: ball-and-stick representation of a double chain of MoO_4^{2-} oxoanions and *trans*-$(CH_3)_2Sn^{2+}$ linkers. Bottom: schematic view of the crystal packing of compound **1** along the crystallographic *b* axis. For clarity, hydrogen and oxygen atoms have been omitted, resulting in the structural skeleton.

ladder-like diorganotin cluster combined with oxometalate anions and, more interestingly, the first example in which this type of cluster is involved in a 2-dimensional network, as all previously reported compounds display a discrete molecular character.

The crystal packing of compound **2** shows hybrid organic−inorganic layers parallel to the (1,0,$\bar{1}$) plane formed by $[\{(CH_3)_2Sn\}_4O_2]^{2+}$ subunits linked to four neighboring ladder-like clusters through four orthomolybdate anions. Each molybdate is connected to one $[\{(CH_3)_2Sn\}_4O_2]^{2+}$ subunit acting as a μ^2-O bridge between endo- and exocyclic Sn centers via the O2 atom and to the other as a monodentate ligand to the exocyclic Sn1 via the O3 atom. In addition, the O4 atom is involved in a long intralamellar interaction with an exocyclic Sn1 center (2.889(2) Å), whereas the O5 atom remains unshared. This arrangement leads to a 2-dimensional lattice showing a quasi-planar metal−oxo framework with both the methyl groups and the unshared O atoms pointing outside. The hybrid layers pack along the crystallographic *a* axis with the interlamellar space occupied by the methyl groups in such a way that a sequence of metal−oxo frameworks and hydrophobic regions is formed along this direction (Figure 4). Besides methyl−methyl interactions, the crystal packing is also stabilized by two different types of C3−H3···O5 hydrogen bonds, the C3···O5 distances being 3.512(3) and 3.514(4) Å and the C3−H5−O5 angles 167° and 161°, respectively.

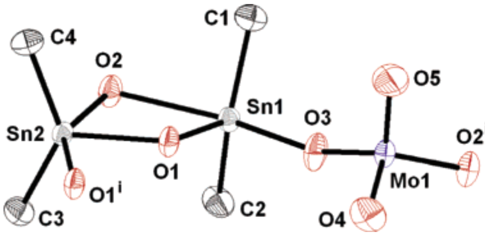

Figure 3. ORTEP view of the asymmetric unit of compound **2** together with the labeling scheme (50% probability displacement ellipsoids; hydrogen atoms have been omitted for clarity). Symmetry codes: (i) $1 - x$, $2 - y$, $2 - z$; (ii) $-1/2 + x$, $3/2 - y$, $-1/2 + z$.

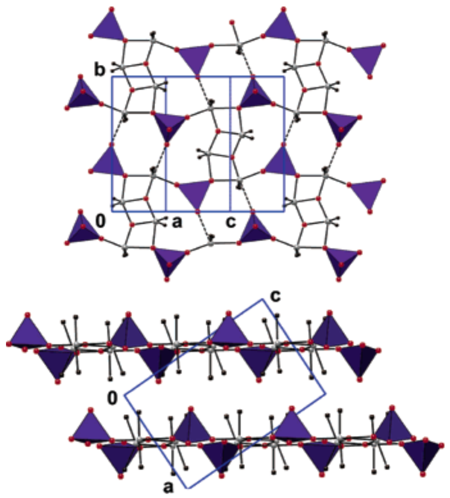

Figure 4. Top: projection of a hybrid layer of MoO_4^{2-} oxoanions and $[\{(CH_3)_2Sn\}_4O_2]^{2+}$ tetramers on the (1,0,$\bar{1}$) plane. Bottom: view of the crystal packing of compound **2** along the crystallographic *b* axis. Hydrogen atoms have been omitted for clarity.

Crystal Structure of Compound 3. Compound **3** crystallizes in the orthorhombic space group *Pbcm* with one Mo atom and one Sn atom in the asymmetric unit (Figure 5). The crystal structure contains polymeric $\{[Mo_2O_7(H_2O)_2]^{2-}\}_\infty$ polyanions connected in a 2-dimensional network by *trans*-$(CH_3)_2Sn^{2+}$ moieties. The polymeric $\{[Mo_2O_7(H_2O)_2]^{2-}\}_\infty$ polyanion consists of a zigzag chain formed by corner-shared $[Mo_2O_8(H_2O)_2]$ dimeric subunits which result from association of two edge-shared octahedra. In contrast to those in compounds **1** and **2**, the Mo center in **3** has a distorted octahedral coordination environment with five oxo ligands:

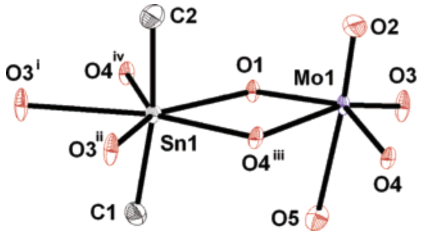

Figure 5. ORTEP view of the asymmetric unit of compound **3** together with the labeling scheme (50% probability displacement ellipsoids; hydrogen atoms have been omitted for clarity). Symmetry codes: (i) $1 + x, y, 3/2 - z$; (ii) $1 + x, y, z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1 - x, 1 - y, 1/2 + z$.

two *cis*-related terminal oxo ligands (axial O2 and equatorial O3), two bridging oxo ligands between edge-shared octahedra (equatorial O4 and O4^{ii}), and one bridging oxo ligand between corner-shared octahedra (equatorial O1). The coordination sphere is completed by a water molecule occupying an axial position (O5). The equatorial Mo−O bond lengths range from 1.728(3) Å for O3 to 2.151(3) Å for O4^{ii}, the axial bond lengths being 1.695(4) Å for O2 and 2.459(3) Å for the water molecule O5. To our knowledge, this type of infinite arrangement has not been observed before, and therefore, the $\{[Mo_2O_7(H_2O)_2]^{2-}\}_\infty$ unit constitutes a new polyanion fragment among the numerous polymeric polyoxomolybdates described to date.[17]

Interestingly, the Sn atom is 7-coordinated and shows a distorted pentagonal-bipyramidal $(CH_3)_2SnO_5$ coordination geometry with the methyl groups occupying relative *trans* positions. The Sn−C bond lengths and the C−Sn−C bond angle are similar to those determined for compound **1**, whereas the equatorial bonding can be described as three long (2.236(5), 2.243(2), and 2.243(2) Å) and two very long (2.426(3) Å) Sn−O bonds (Table 2). This type of coordination is not common for dimethyltin(IV) groups, as it has only been observed in our previously reported tetrameric dimethyltin-containing tungstoarsenate(III).[7b]

The crystal packing of compound **3** displays $\{[Mo_2O_7(H_2O)_2]^{2-}\}_\infty$ polyanions arranged parallel to each other along the [010] direction and linked through *trans*-$(CH_3)_2Sn^{2+}$ moieties coordinated to the terminal O3 atoms of one polyanion and to the bridging O atoms of the adjacent polyanion. In this way, hybrid organic−inorganic layers parallel to the *ac* plane are formed, which pack along the crystallographic *b* axis with the methyl groups pointing to the interlamellar space (Figure 6). Hydration water molecules (O6) are located between the layers, so that they are held together by means of an extended network of strong O−H···O hydrogen bonds involving both the coordinated O5 water molecules and the unshared O2 terminal atoms, the O6···O5 and O6···O2 distances being 2.860(5) and 2.898(6) Å, respectively.

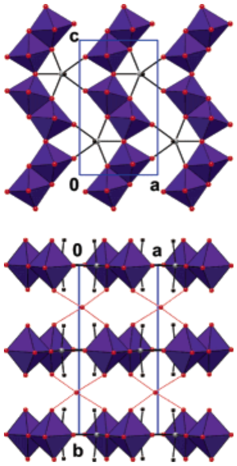

Figure 6. Top: projection of a hybrid layer of polymeric $\{[Mo_2O_7(H_2O)_2]^{2-}\}_\infty$ polyanions linked by *trans*-$(CH_3)_2Sn^{2+}$ moieties on the (010) plane. Bottom: view of the crystal packing of compound **3** along the crystallographic *c* axis. Hydrogen atoms have been omitted for clarity.

Conclusions

Our work has shown that three different compounds can be isolated as single crystals suitable for X-ray diffraction studies from the reaction of $(CH_3)_2SnCl_2$ with Na_2MoO_4 in an aqueous medium in different pH ranges. All these compounds show hybrid organic−inorganic extended assemblies based on molybdate anions linked by $(CH_3)_2Sn^{2+}$ organometallic moieties to give 2- or 3-dimensional lattices. Furthermore, compound **2** constitutes the first example of a layered structure incorporating dimeric tetraorganodistannoxane subunits, whereas the $\{[Mo_2O_7(H_2O)_2]^{2-}\}_\infty$ polyanion observed in compound **3** represents a new type of polymeric polyoxomolybdate. It is interesting to underline that the Sn(IV) center expands its coordination number from 5 to 7 and the methyl groups move from relative *cis* to *trans* positions on going from basic to highly acidic synthetic conditions. Therefore, this family of compounds can be considered as a beautiful example of the unique linking ability of the $(CH_3)_2Sn^{2+}$ electrophile, since they show that the Sn(IV) center can adopt different coordination geometries depending on the requirements imposed by the crystal packing. Currently, we are carrying out analogous investigations on the reactivity of the $(CH_3)_2Sn^{2+}$ moiety toward isopolytungstates and −vanadates, and we plan to extend this work to other mono-, di-, or triorganotin electrophiles to obtain a wider family of species which could be of interest for catalytic applications.

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Supporting Information Available: Figures of infrared spectra and thermograms for compounds **1**−**3** and X-ray crystallographic file of compounds **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) See for example: (a) Armour, A. W.; Drew, M. G. B.; Mitchell, P. C. H. *J. Chem. Soc., Dalton Trans*. **1975**, 1493. (b) Seleborg M. *Acta Chem. Scand*. **1967**, *21*, 499. (c) Gatehouse, B. M.; Leverett, P. *J. Chem. Soc., Dalton Trans*. **1976**, 1316. (d) Range, K. J.; Fässler A. *Acta Crystallogr*. **1975**, *B31*, 1451. (e) Toraya, H.; Marumo, F.; Yamase, T. *Acta Crystallogr*. **1984**, *B40*, 145. (f) Gatehouse, B. M.; Leverett, P. *J. Chem. Soc. A* **1968**, 1398.