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13-Tungstoborate Stabilized by an Organostannoxane Hexamer

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The novel dimethyltin-containing polyanion $[\{(CH_3)_2Sn\}_6(OH)_2O_2(H_2BW_{13}O_{46})_2]^{12-}$ (**1**) is composed of two $[H_2BW_{13}O_{46}]^{9-}$ clusters linked by an unprecedented planar, hexameric $[\{(CH_3)_2Sn\}_6(OH)_2O_2]^{8+}$ organostannoxane moiety, representing the first X-ray structural characterization of a molecular hybrid organic–inorganic tungstoborate and of the elusive $[H_nBW_{13}O_{46}]^{(11-n)-}$ species.

Polyoxometalates (POMs) are discrete anionic metal−oxygen clusters with a multitude of interesting structures, compositions, properties, and potential applications in different fields including catalysis, materials science, and medicine.[1] Functionalization of lacunary POM precursors with covalently attached organometallic moieties has significantly enriched this field over the past years. Among these moieties, mono-organotin species constitute one of the most widely studied derivatizing agents because of the relatively high stability of the Sn−C bond in aqueous media and also the fact that Sn^{IV} can substitute addenda sites in POM frameworks.[2] Recently, our group[3] has demonstrated that also di-organotin electrophiles (e.g., $(CH_3)_2Sn^{2+}$) can act as linkers of heteropolytungstates or isopolymetalates. This work has resulted in discrete, molecular assemblies with unprecedented architectures (from dimers to dodecamers), multi-dimensional materials, and also the stabilization of polyoxotungstate fragments not observed before.

Now we decided to investigate the reactivity of the $(CH_3)_2Sn^{2+}$ electrophile toward main group III heteropolytungstates, and in particular tungstoborates. This class of POMs has been studied much less than those containing heteroatoms from main groups IV and V. A relatively small number of structurally characterized tungstoborates can be found in the literature.[4] Most of these POMs contain the $[BW_{12}O_{40}]^{5-}$ Keggin polyanion, but other examples include $[HBW_{11}O_{39}]^{8-}$, $[B_3W_{39}O_{132}]^{21-}$, $[H_4BW_{20}O_{66}]^{11-}$, $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (Ln: Ce, Eu), $[Ce(H_2O)_3(BW_{11}O_{39})]^{6-}$, and $[BW_{11}O_{39}\{Co(H_2O)\}]^{6-}$.

Here we report on the dimethyltin-containing 13-tungstoborate $[\{(CH_3)_2Sn\}_6(OH)_2O_2(H_2BW_{13}O_{46})_2]^{12-}$ (**1**, see Figure 1), which was isolated as the potassium salt $K_{12}[\{(CH_3)_2Sn\}_6(OH)_2O_2(H_2BW_{13}O_{46})_2]\cdot 32H_2O$ (**1a**).

Compound **1a** was first obtained from the reaction of a $[HBW_{11}O_{39}]^{8-}$ precursor[5] and $(CH_3)_2SnCl_2$ (1:2 ratio) in aqueous 1 M KCl at pH 4.[6] However, this procedure led to low yields and poor reproducibility, so a more rational

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(5) $K_8[HBW_{11}O_{39}]\cdot 13H_2O$ was synthesized according to ref 4e.

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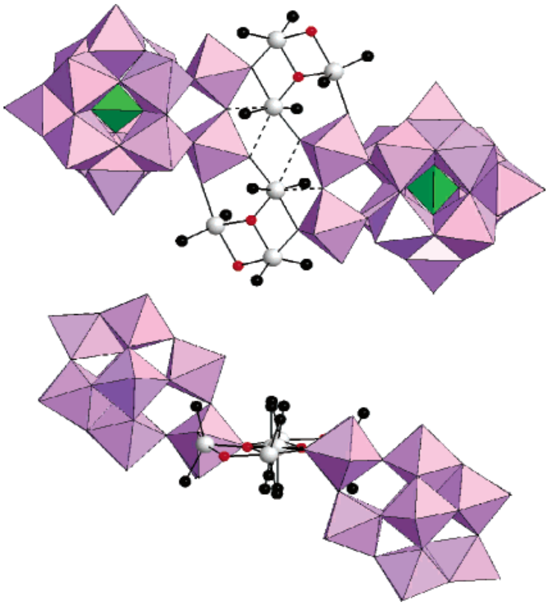

Figure 1. Combined polyhedral/ball-and-stick representations of polyanion **1** (upper, top view; lower, side view). Color code: WO_6 octahedra (lilac), BO_4 tetrahedra (green), C (black), O (red), and Sn (gray).

synthesis was accomplished by reacting $(CH_3)_2SnCl_2$, Na_2WO_4, and $[HBW_{11}O_{39}]^{8-}$ (3:2:1 ratio) in the same 1 M KCl medium at pH 4.7.[7]

Polyanion **1** constitutes the first discrete, molecular hybrid organic−inorganic tungstoborate reported. Single-crystal XRD[8] reveals that the sandwich-type structure of **1** is composed of two $[H_2BW_{13}O_{46}]^{9-}$ units linked by a central hexameric $[\{(CH_3)_2Sn\}_6(OH)_2O_2]^{8+}$ organostannoxane moiety, resulting in an assembly with C_i symmetry (see Figures 1 and 2).

The $[H_2BW_{13}O_{46}]^{9-}$ fragment is comprised of a monolacunary $[HBW_{11}O_{39}]^{8-}$ α-Keggin subunit onto which a (HW_2O_{11}) group of two corner-sharing WO_6 octahedra is attached. This dimeric tungsten−oxo group is grafted to the vacant site of the BW_{11} subunit with each WO_6 octahedron connected via corner-sharing to two octahedra that surround the "lacuna" in such a way that the $[HBW_{11}O_{39}]^{8-}$ subunit acts as a *bis*(bidentate) bridge between the two extra W centers (W12 and W13). Therefore, W12 and W13 are each coordinated to three W−O−W oxo bridges, one between both tungstens (O123) and two with the monolacunary subunit (O112 and O612 for W12; O103 and O713 for W13). The coordination spheres are completed by terminal and bridging (W−O−Sn) oxygens. The connectivity to the organostannoxane moiety is different for W12 and W13: the former shows two cis-related terminal oxo ligands (O12T and O12B) and a bridging one (O12A), whereas the latter displays one terminal (O13T) and two bridging O atoms (O13S and O13R). Such a BW_{13} Keggin unit has already been observed by Tézé et al. in 1997 in the trimeric $[B_3W_{39}O_{132}]^{21-}$,[4e] and the same authors also showed that $[H_3BW_{13}O_{46}]^{8-}$ is metastable in acidic solution (1 < pH < 5), but they could not isolate this ion in the solid state. Very recently Cadot and co-workers reinvestigated the solution chemistry of Tézé's $[B_3W_{39}O_{132}]^{21-}$, and in this context they isolated some condensation derivatives based on BW_{13}, such as the monocapped $[H_3BW_{14}O_{48}]^{6-}$, the dimeric $[H_6B_2W_{26}O_{90}]^{12-}$, and Tézé's trimeric $[H_6B_3W_{39}O_{132}]^{15-}$.[9] Thus, the $[H_nBW_{13}O_{46}]^{(11-n)-}$ species has been lacking detailed struc-

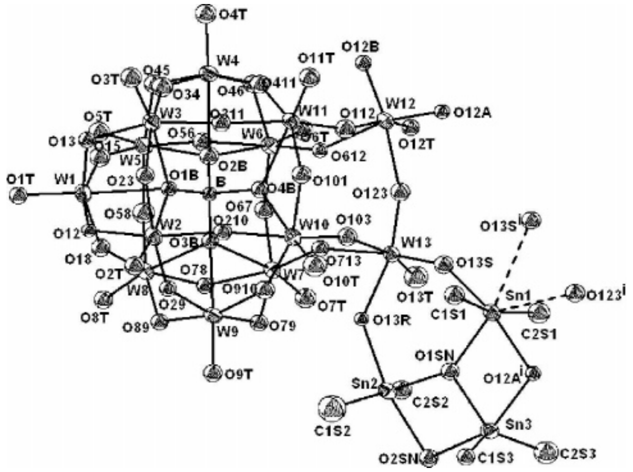

Figure 2. ORTEP view of the asymmetric unit of the centrosymmetric polyanion **1** with atom labeling (50% probability displacement ellipsoids; H atoms have been omitted for clarity). Symmetry codes: (i) $1 - x, -y, 1 - z$. Selected bond lengths (Å): W12−O12B, 1.752(15); W12−O12T, 1.783(16); W12−O12A, 1.856(15); W12−O612, 2.009(15); W12−O123, 2.120(16); W12−O112, 2.135(17); W13−13T, 1.754(19); W13−O13S, 1.805(17); W13−O123, 1.824(16); W13−O713, 2.060(16); W13−O13R, 2.097(14); W13−O103, 2.150(16); W11−O112, 1.783(17); W10−O103, 1.786(17); W6−O612, 1.855(15); W7−O713, 1.801(15); B-O1B, 1.50(3); B-O2B, 1.48(3); B-O3B, 1.49(3); B-O4B, 1.58(3); Sn1−O1Sn, 2.092(15); Sn1−C2S1, 2.10(3); Sn1−C1S1, 2.11(2); Sn1−O13S, 2.163(17); Sn1−O12A^i, 2.262(15); Sn1−O123^i, 2.74(2); Sn1−O13S^i, 2.86(2); Sn2−O1Sn, 2.022(16); Sn2−C1S2, 2.09(3); Sn2−C2S2, 2.14(2); Sn2−O13R, 2.177(14); Sn2−O2Sn, 2.240(17); Sn3−C2S3, 2.06(3); Sn3−O1Sn, 2.086(17); Sn3−C1S3, 2.12(2); Sn3−O2Sn, 2.161(16); Sn3−O12A^i, 2.213(14).

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(6) To a solution of $(CH_3)_2SnCl_2$ (0.088 g, 0.4 mmol) in aqueous 1 M KCl (30 mL) solid $K_8[HBW_{11}O_{39}]\cdot 13H_2O$ (0.642 g, 0.2 mmol) was added. The reaction mixture (pH 4.0) was heated at ∼70 °C for 30 min. After cooling down to room temperature, aqueous 1 M NaCl solution (2.5 mL) was added to the resulting clear solution. Plate-like colorless crystals suitable for X-ray diffraction were formed in a few days by slow evaporation of the solvent at room temperature.

(7) Synthesis of **1a**: To a solution of $Na_2WO_4\cdot 2H_2O$ (0.132 g, 0.4 mmol) and $(CH_3)_2SnCl_2$ (0.132 g, 0.6 mmol) in aqueous 1 M KCl (30 mL) solid $K_8[HBW_{11}O_{39}]\cdot 13H_2O$ (0.642 g, 0.2 mmol) was added. The reaction mixture (pH 4.7) was heated at ∼70 °C for 30 min, leading to a cloudy solution which was filtered while hot and then left for evaporation of the solvent in an open beaker. Compound **1a** was obtained overnight as a crystalline powder (yield: 0.322 g, 39% based on Sn). Anal. Calcd (found) for $C_{12}H_{106}B_2K_{12}O_{128}Sn_6W_{26}$: C, 1.74 (1.62); H, 1.29 (1.27); B, 0.26 (0.20); K, 5.67 (5.50), Sn, 8.60 (8.74), W, 57.7 (58.1). IR. (KBr pellets, cm^{-1}): 1229(w), 1203(sh), 1065(sh), 968(m), 952(s), 902(s), 835(vs), 780(vs), 769(sh), 742(sh), 636(m), 549(sh), 517(m), 451(w). TGA/DSC. Decomposition starts at room temperature with a dehydration step comprising three highly overlapping endothermic processes. This step involves the release of ∼32 water molecules below 210 °C [found: 7.09; calcd: 6.96], and just above this temperature, loss of the methyl groups takes place in two highly overlapping exothermic processes. Decomposition ends at 390 °C, but a thermally stable residue is only observed at temperatures above 570 °C [calcd (found) for $B_2K_{12}O_{99}Sn_6W_{26}$: 91.37 (91.40)].

(8) Crystal data for **1a**: $C_{12}H_{106}B_2K_{12}O_{128}Sn_6W_{26}$, fw = 8282.0 g·mol^{-1}, triclinic, $P\bar{1}$ space group; $a = 12.2644(8)$ Å, $b = 13.0387(12)$ Å, $c = 23.392(2)$ Å, $\alpha = 91.952(5)°$, $\beta = 96.536(5)°$, $\gamma = 111.559(4)°$, $V = 3444.7(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 4.015$ g·cm^{-3}, $\mu = 23.144$ mm^{-1}; 93 894 collected reflns, 14 054 unique ($R_{int} = 0.191$), 7770 observed [$I > 2\sigma(I)$]; 490 params, $R(F) = 0.065$ [$I > 2\sigma(I)$], $wR(F)^2 = 0.180$ (all data), GOF = 1.008; Bruker X8 APEX II CCD diffractometer, $T = 173(2)$ K, λ(Mo Kα) = 0.71073 Å.

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tural analysis ever since its discovery 10 years ago. Our results show that the BW_{13} unit can be stabilized by organotin moieties.

The W−O bond lengths of the $[HBW_{11}O_{39}]^{8-}$ subunit in **1** are not unusual, but it exhibits a distorted central BO_4 tetrahedron with three short bonds and a long one (B−O4B). On the other hand, the W−O bonding for both W12 and W13 can be described as four alternating, trans-related short and long bonds O12B−W12−O123−W13−O13R. This type of distortion is also observed starting from both O12T and O13T, so that an analogous long−short bond sequence propagates along the monolacunary Keggin skeleton, ending at O1T opposite to the vacant site. According to elemental and thermogravimetric analyses, the tungstoborate cluster in **1** is diprotonated. This is consistent with the bond valence sum calculation,[10] which indicates two protonation sites: the W13−O13R−Sn2 bridge and the central μ_3-O4B atom, the proton therefore being directed to the center of the vacant position. Tézé noted that the $[HBW_{11}O_{39}]^{8-}$ precursor contains a single proton that cannot be neutralized without destruction of the polyanion.[4e]

The previously reported $[BW_{13}O_{46}]^{11-}$ cluster has three terminal O atoms (*fac* isomer) for both W centers belonging to the grafted dimeric fragment.[4e] Thus, this tungstoborate violates the Lipscomb rule,[11] but nevertheless, its existence in solution in the triprotonated form $[H_3BW_{13}O_{46}]^{8-}$ was demonstrated by Tézé et al., based on polarography and ultracentrifugation.[4e] Consistent with our observations for **1**, it could be proposed that two of the three protons are disordered over the terminal oxo ligands of the grafted dimer in order to fulfill the Lipscomb rule, whereas the third one is located on the unsaturated central O atom of the BO_4 hetero group.

We have used the stabilizing capability[3f] of the $(CH_3)_2Sn^{2+}$ electrophile to isolate the target 13-tungstoborate cluster, and therefore, polyanion **1** represents the first structural characterization of the elusive $[H_nBW_{13}O_{46}]^{(11-n)-}$ species. Furthermore, the central $[\{(CH_3)_2Sn\}_6(OH)_2O_2]^{8+}$ subunit of **1** constitutes an unprecedented organostannoxane moiety. It is composed of an inner, rhombic Sn_2O_2 cyclic core of two Sn centers (Sn1) related by a center of inversion and bridged in an asymmetric fashion by the $[H_2BW_{13}O_{46}]^{9-}$ clusters through the O13S/O13S^i atoms. The Sn1 atom is seven-coordinate with a distorted pentagonal-bipyramidal $(CH_3)_2SnO_5$ geometry where the methyl groups occupy the apical positions in a relative trans arrangement. The equatorial plane is formed by four O atoms belonging to the tungstoborates (O13S, O13S^i, O123^i, and O12A^i) and an oxo ligand (O1Sn) acting as a tridentate bridge by coordinating the two Sn centers of an outer Sn_2O_2 cyclic unit. The Sn−C bond lengths (see caption of Figure 2 for detailed values) and the C−Sn−C angle (164.9(10)°) are similar to those observed for other *trans*-$(CH_3)_2SnO_5$ moieties,[3b,e] whereas the equatorial bonding can be described as two short, one long, and two very long Sn−O bonds.

The outer Sn_2O_2 cyclic unit contains two crystallographically independent Sn atoms (Sn2 and Sn3) which are both five-coordinate and exhibit highly distorted trigonal-bipyramidal $(CH_3)_2SnO_3$ geometries. In both cases, the equatorial plane is defined by the μ_3-O1Sn bridge and the two methyl groups, which therefore display a relative cis arrangement, whereas one of the apical positions is occupied by the μ_2-O2Sn atom, which bridges both Sn centers and is protonated according to the bond valence sum calculation. The coordination spheres are completed by the O13R hydroxo group for Sn2 and the O12A^i atom for Sn3, which therefore, is doubly connected to Sn1. All the Sn−C and Sn−O bonds are short with the exception of Sn2−O2Sn and Sn3−O12A, and therefore, the sequence of alternating short and long trans-related bonds described for the grafted dimer of the tungstoborate cluster is extended along the apical bonding of the outer Sn_2O_2 cycle. On the other hand, the axial O−Sn−O (Sn2, 165.8(6)°; Sn3, 153.0(6)°) and equatorial C−Sn−C bond angles (Sn2, 141.9(11)°; Sn3, 131.1(11)°) deviate significantly from the ideal geometry, a common fact also observed for other *cis*-$(CH_3)_2SnO_3$ moieties.[3e,f]

The $[\{(CH_3)_2Sn\}_6(OH)_2O_2]^{8+}$ subunit displays an almost planar tin−oxo framework with the methyl groups pointing above and below. The distances of the atoms to the idealized plane defined by the Sn−O skeleton range from 0.026(16) Å for O13S to 0.629(12) Å for O13R. Thus, the butterfly structure of **1** exhibits two lateral hydrophilic domains, provided by the tungstoborate clusters, and a central hydrophobic area defined by the organotannoxane methyl groups.

In summary, our work has demonstrated that the $(CH_3)_2Sn^{2+}$ electrophile is reactive toward main group III heteropolytungstates, resulting in polyanion **1**, which constitutes the first discrete, molecular hybrid organic−inorganic tungstoborate reported. Polyanion **1** is composed of two $[H_2BW_{13}O_{46}]^{9-}$ clusters linked by an unprecedented hexameric, planar $[\{(CH_3)_2Sn\}_6(OH)_2O_2]^{8+}$ organostannoxane moiety. The stabilizing capability of the $(CH_3)_2Sn^{2+}$ group has allowed us to structurally characterize the elusive $[H_nBW_{13}O_{46}]^{(11-n)-}$ species for the first time. We plan to extend this work to other main group III heteropolytungstates and to other eletrophiles in order to achieve a better understanding of the reactivity of this relatively unknown family of POMs. Furthermore, we plan to directly detect the most likely inert proton associated with each of the BO_4 hetero groups in **1** by NMR and/or neutron diffraction.

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Supporting Information Available: Fourier transform IR spectrum and thermogravimetric analysis/differential scanning calorimetry curves of **1a** and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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