

## A Novel Hexatungstate Fragment Stabilized by Dimethyltin Groups:



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Received October 16, 2006

Reaction of  $Na_2WO_4$  and  $(CH_3)_2SnCl_2$  in water (pH 7) led to the formation of the hybrid organic–inorganic polyanion  $[\{(CH_3)_2Sn\}_2(W_6O_{22})]^{4-}$  (**1**), which is composed of a novel hexatungstate core stabilized by two dimethyltin groups. Selective crystallization of **1** with guanidinium cations resulted in  $[C(NH_2)_3]_4[\{(CH_3)_2Sn\}_2(W_6O_{22})] \cdot 2H_2O$  (**1a**), which exhibits a 1D arrangement via distorted trigonal-bipyramidal *cis*- $(CH_3)_2SnO_3$  moieties.

Polyoxometalates (POMs) are anionic metal–oxygen clusters with enormous compositional, structural, and electronic versatility and a multitude of interesting properties and potential applications in different fields including catalysis, materials science, and medicine.<sup>1</sup> The chemistry of POMs has been significantly enriched over the past few years by their functionalization with covalently attached organometallic moieties in an effort to improve their selectivity to specific targets. In particular, organotin species have been widely studied as derivatizing agents because of the stability of the Sn–C bond and also the fact that  $Sn^{IV}$  can substitute for addenda metals in POM skeletons. Thus, several examples of monomeric or dimeric monoorganotin-containing heteropolytungstates have been reported, predominantly by the Pope,<sup>2</sup> Knoth,<sup>3</sup> Liu,<sup>4</sup> and Hasenknopf<sup>5</sup> groups. In addition, we have demonstrated that diorganotin electrophiles can act as highly efficient linkers of lacunary heteropolytungstates to construct assemblies with unprec-

edented architectures. These include discrete molecular dimeric species, tetrameric cage-like assemblies, dodecameric superlarge POMs, and 2D materials.<sup>6</sup>

Recently, we have described a series of hybrid materials obtained from the interaction of  $(CH_3)_2Sn^{2+}$  with  $MoO_4^{2-}$  ions in water at different pH ranges.<sup>7</sup> Now, we have extended this study to the reactivity of  $(CH_3)_2Sn^{2+}$  toward  $WO_4^{2-}$  ions.

Here we report the synthesis and crystal structure of the first dimethyltin-containing isopolytungstate,  $[\{(CH_3)_2Sn\}_2(W_6O_{22})]^{4-}$  (**1**; see Figure 1), which was isolated as the dihydrated guanidinium salt  $[C(NH_2)_3]_4[\{(CH_3)_2Sn\}_2(W_6O_{22})] \cdot 2H_2O$  (**1a**).

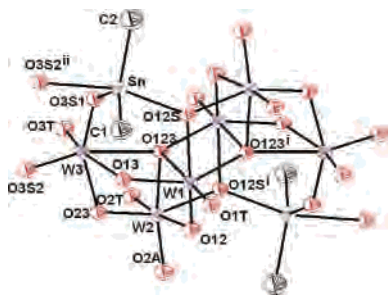
Compound **1a** was obtained from the reaction of  $Na_2WO_4$  and  $(CH_3)_2SnCl_2$  (3:1 ratio) in water at room temperature and neutral pH conditions.<sup>8</sup> Interestingly, **1** could only be isolated as a guanidinium ( $[C(NH_2)_3]^+$ ) salt. The addition of any alkali cation to the reaction mixture resulted in crystals of the corresponding well-known paratungstate-B<sup>9</sup> ( $[H_2W_{12}O_{42}]^{10-}$ ) on the basis of IR spectroscopy. Similar results were obtained when the reaction was carried out at ca. 70 °C, with W:Sn ratios of 2:1 and 4:1, or at values in the range of pH 6–8.

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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. *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.

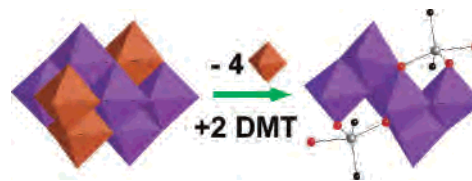
- (2) (a) Zonnevillje, F.; Pope, M. T. *J. Am. Chem. Soc.* **1979**, *101*, 2211. (b) Xin, F.; Pope, M. T. *Organometallics* **1994**, *13*, 4881. (c) Xin, F.; Pope, M. T. *Inorg. Chem.* **1996**, *35*, 5693. (d) Xin, F.; Pope, M. T.; Long, G. J.; Russo, U. *Inorg. Chem.* **1996**, *35*, 1207. (e) Sazani, 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.* **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.* **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) 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.
- (7) Reinoso, S.; Dickman, M. H.; Reicke, M.; Kortz, U. *Inorg. Chem.* **2006**, *45*, 9014.



**Figure 1.** ORTEP view of the centrosymmetric building block **1** with atom labeling (50% probability displacement ellipsoids; methyl H atoms have been omitted for clarity). Bond lengths (Å): W1–O1T, 1.722(6); W1–O12, 1.794(8); W1–O13, 1.837(4); W1–O123<sup>i</sup>, 1.988(5); W1–O12S, 2.134(8); W1–O123, 2.371(5); W2–O2T, 1.735(6); W2–O2A, 1.760(7); W2–O23, 1.923(5); W2–O12S<sup>i</sup>, 1.931(5); W2–O12, 2.277(6); W2–O123, 2.196(6); W3–O3T, 1.729(6); W3–O3S2, 1.758(4); W3–O3S1, 1.859(8); W3–O23, 1.984(8); W3–O13, 2.185(5); W3–O123, 2.242(4); Sn–O3S1, 2.019(7); Sn–C2, 2.106(12); Sn–C1, 2.111(9); Sn–O12S, 2.160(8); Sn–O3S2<sup>ii</sup>, 2.207(4). Symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (ii)  $-x, y, \frac{1}{2} - z$ .

The presence of the  $(\text{CH}_3)_2\text{Sn}^{2+}$  moiety in **1a** can be established unambiguously by a single IR peak of low intensity at  $1197\text{ cm}^{-1}$  (see Figure S1 in the Supporting Information), which is characteristic of the  $\delta_s(\text{CH}_3)$  vibration in methyltin(IV) derivatives. On the other hand, the bands of strong intensity in the region  $3100\text{--}3500\text{ cm}^{-1}$  and at  $1657\text{ cm}^{-1}$  are due to the  $\nu(\text{N-H})$  and  $\delta(\text{NH}_2)$  vibrations of the  $[\text{C}(\text{NH}_2)_3]^+$  cations, respectively, while those below  $1000\text{ cm}^{-1}$  can be attributed to the metal–oxygen stretching and bending modes.<sup>10</sup> Thermal analysis under a  $\text{N}_2$  atmosphere (see Figure S2 in the Supporting Information) shows that **1a** decomposes via three highly overlapping endothermic mass loss steps. The first one is a dehydration process below  $185\text{ }^\circ\text{C}$  [calcd (found) for  $2\text{H}_2\text{O}$ : 1.78% (1.71%)], followed by the release of the four  $[\text{C}(\text{NH}_2)_3]^+$  cations together with two O atoms [calcd (found) for  $\text{C}_4\text{H}_{24}\text{N}_{12}\text{O}_2$ : 13.42% (13.22%)]. This process takes place below  $330\text{ }^\circ\text{C}$ , after which **1a** undergoes loss of the methyl groups and two additional O atoms [calcd (found) for  $\text{C}_4\text{H}_{12}\text{O}_2$ : 4.54% (4.77%)]. Decomposition ends at  $470\text{ }^\circ\text{C}$ , but just above this temperature, an increase of mass takes place, leading to a stable phase at  $620\text{ }^\circ\text{C}$  [calcd (found) for  $\text{Sn}_2\text{W}_6\text{O}_{20}$ : 81.84% (82.4%)].

Single-crystal X-ray diffraction (XRD)<sup>11</sup> revealed that **1a** crystallizes in the monoclinic space group  $C2/c$ , with the asymmetric unit being composed of half of the centrosymmetric building block **1** (see Figure 1), two  $[\text{C}(\text{NH}_2)_3]^+$  cations, and one water molecule of hydration. The polyanionic building block **1** is composed of two  $(\text{CH}_3)_2\text{Sn}^{2+}$  groups



**Figure 2.** Structural relation between the parent  $\text{M}_{10}\text{O}_{28}$  cluster (left) and **1** (right). DMT:  $(\text{CH}_3)_2\text{Sn}^{2+}$  moiety.

covalently attached to a novel type of hexatungstate fragment,  $(\text{W}_6\text{O}_{22})^{8-}$ , resulting in the first structurally characterized dimethyltin-containing isopolytungstate.

A rather small number of isopolytungstates have been reported in the literature.<sup>1a,12</sup> The structures of those species based on exclusive edge-shared  $\text{WO}_6$  octahedra can all be formally derived from the parent  $\text{M}_{10}\text{O}_{28}$  decametalate cluster.<sup>13</sup> To date, the structures of only two hexatungstates are known, namely, Lindqvist's  $[\text{W}_6\text{O}_{19}]^{2-}$ <sup>14</sup> and Hartl's  $[\text{H}_3\text{W}_6\text{O}_{22}]^{5-}$ .<sup>12a</sup> The former has a well-known  $O_h$  structure, whereas the latter is a  $C_s$  assembly derived from the  $\text{M}_{10}\text{O}_{28}$  framework by removal of four  $\text{WO}_6$  octahedra from the central part of the POM. In contrast, the  $(\text{W}_6\text{O}_{22})^{8-}$  fragment present in **1** has  $C_i$  symmetry and may be obtained by removal of two diagonally related pairs of  $\text{WO}_6$  octahedra from the  $\text{M}_{10}\text{O}_{28}$  framework (see Figure 2).

The  $(\text{W}_6\text{O}_{22})^{8-}$  fragment in **1** is unprecedented and can be described as two fused  $\text{W}_3\text{O}_{13}$  trimers linked via edge sharing of  $\text{WO}_6$  octahedra. This hexatungstate assembly in **1** corresponds exactly to the geometric form 15 of the possible 18 compiled by Tytko and Glemser in 1971.<sup>15</sup> The bond lengths in **1** are in the range  $1.722(6)\text{--}1.859(8)\text{ \AA}$  for terminal  $\text{W}\text{--}\text{O}$  bonds,  $1.794(8)\text{--}2.185(5)\text{ \AA}$  for  $\text{W}\text{--}\mu_2\text{--}\text{O}(\text{W})$  bridges, and  $1.988(5)\text{--}2.371(5)\text{ \AA}$  for  $\text{W}\text{--}\mu_4\text{--}\text{O}(\text{W})$  bonds. These are not unusual for isopolytungstates, except for the  $\text{W3}\text{--}\text{O3S1}$  bond, which is longer than expected because of coordination to the Sn center. Close inspection of the  $(\text{W}_6\text{O}_{22})^{8-}$  fragment in **1** reveals that each of the three pairs of W centers exhibits a different number of terminal bonds: one for W1, two (*cis*-related) for W2, and three (*fac* isomer) for W3 (see Figure 1). Thus, this hexatungstate violates the Lipscomb rule,<sup>16</sup> but its possible existence in solution cannot be a priori ruled out completely.

At around pH 6, the two predominant isopolytungstate species in equilibrium are paratungstate-B and paratungstate-

(8) Synthesis of **1a**:  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (0.99 g, 3 mmol) and  $(\text{CH}_3)_2\text{SnCl}_2$  (0.22 g, 1 mmol) were dissolved in water (30 mL), and the solution (pH 7.2) was stirred for 30 min at room temperature. The addition of a few drops of aqueous 1 M  $[\text{C}(\text{NH}_2)_3]\text{Cl}$  and slow evaporation at room temperature led to colorless, blocklike single crystals suitable for XRD after a few days. Alternatively, **1a** can also be isolated as a bulk powder (yield: 0.55 g, 54% based on W) by adding solid  $[\text{C}(\text{NH}_2)_3]\text{Cl}$  (0.19 g, 2 mmol). Anal. Calcd (found) for  $\text{C}_8\text{H}_{40}\text{N}_{12}\text{O}_{24} \cdot \text{Sn}_2\text{W}_6$ : C, 4.74 (4.76); H, 1.99 (2.02); N, 8.28 (8.27); Sn, 11.70 (11.1); W, 54.37 (53.0). IR (KBr pellets,  $\text{cm}^{-1}$ ): 3410(vs), 3246(s), 3171(s), 1657(s), 1568(m), 1197(w), 945(s), 871(s), 835(s), 752(s), 644(vs), 554(m), 538(m), 522(m), 468(m).

(9) Allmann, R. *Acta Crystallogr.* **1971**, B27, 1393.

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

(11) Crystal data for **1a**:  $\text{C}_8\text{H}_{40}\text{N}_{12}\text{O}_{24}\text{Sn}_2\text{W}_6$ , fw = 2028.9  $\text{g}\cdot\text{mol}^{-1}$ , monoclinic,  $C2/c$  space group;  $a = 23.597(2)\text{ \AA}$ ,  $b = 10.2926(8)\text{ \AA}$ ,  $c = 19.713(3)\text{ \AA}$ ,  $\beta = 125.271(4)^\circ$ ,  $V = 3908.9(7)\text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 3.441\text{ g}\cdot\text{cm}^{-3}$ ,  $\mu = 18.926\text{ mm}^{-1}$ ; 90 482 collected reflections, 6917 unique ( $R_{\text{int}} = 0.116$ ), 5211 observed reflections [ $I > 2\sigma(I)$ ]; 127 parameters,  $R(F) = 0.038$  [ $I > 2\sigma(I)$ ],  $wR(F)^2 = 0.096$  (all data), GOF = 1.046; Bruker X8 Apex II CCD diffractometer,  $T = 173(2)\text{ K}$ ,  $\lambda$  (Mo K $\alpha$ ) = 0.710 73  $\text{\AA}$ .

(12) (a) Hartl, H.; Palm, R.; Fuchs, J. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1492. (b) Fuchs, J.; Palm, R.; Hartl, H. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 2651. (c) Brüdgam, I.; Fuchs, J.; Hartl, H.; Palm, R. *Angew. Chem., Int. Ed.* **1998**, 37, 2668. (d) Himeno, S.; Yoshihara, M.; Maekawa, M. *Inorg. Chem. Commun.* **2001**, 4, 5. (e) Long, D.-L.; Kögerler, P.; Parenty, A. D. C.; Fielden, J.; Cronin, L. *Angew. Chem., Int. Ed.* **2006**, 45, 4798.

(13) Evans, H. T.; Swallow, A. G.; Barnes, W. H. *J. Am. Chem. Soc.* **1964**, 86, 4209.

(14) Fuchs, J.; Freiwald, W.; Hartl, H. *Acta Crystallogr.* **1978**, B34, 1764.

(15) Tytko, K.-H.; Glemser, O. *Z. Naturforsch. B* **1971**, 26, 659.

(16) Lipscomb, W. N. *Inorg. Chem.* **1965**, 4, 132.

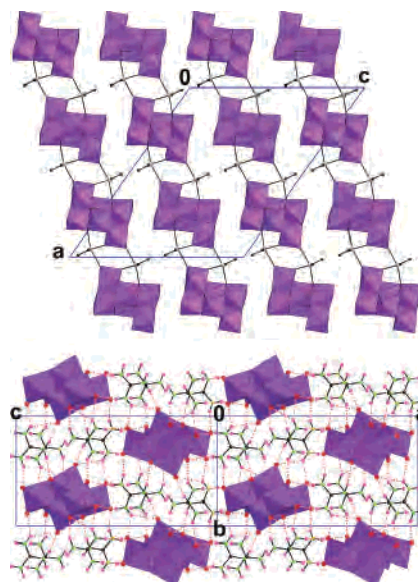
## COMMUNICATION

A<sup>17</sup> ([W<sub>7</sub>O<sub>24</sub>]<sup>6-</sup>), as determined by <sup>183</sup>W NMR spectroscopy.<sup>18</sup> However, the presence of other intermediates appears plausible, as indicated by the group of Hartl.<sup>12a,b</sup> Therefore, we believe that the (W<sub>6</sub>O<sub>22</sub>)<sup>8-</sup> fragment of **1** does actually exist in solution in low concentration, most likely in its diprotonated form to fulfill the Lipscomb rule. In our case, (i) this hexatungstate fragment is stabilized by two (CH<sub>3</sub>)<sub>2</sub>-Sn<sup>2+</sup> groups and (ii) the use of [C(NH<sub>2</sub>)<sub>3</sub>]<sup>+</sup> cations allowed us to selectively crystallize **1**. It must be remembered that with any other alkali cation we always obtained salts of paratungstate-B.

The two (CH<sub>3</sub>)<sub>2</sub>Sn<sup>2+</sup> moieties in **1** are bound to the hexatungstate fragment via the terminal O3S1/O3S1<sup>i</sup> and the bridging O12S/O12S<sup>i</sup> atoms (see Figure 1). The Sn centers are pentacoordinated, and the highly distorted coordination geometry of the *cis*-(CH<sub>3</sub>)<sub>2</sub>SnO<sub>3</sub> unit is best described as trigonal-bipyramidal. The equatorial plane is defined by O3S1 and the two methyl groups, whereas O12S is located in an axial position. The coordination sphere of Sn is completed by a terminal O atom (O3S2<sup>ii</sup>) of an adjacent hexatungstate fragment, thus occupying the remaining axial position. The distortion of the *cis*-(CH<sub>3</sub>)<sub>2</sub>SnO<sub>3</sub> unit is reflected by the long Sn–O3S2<sup>ii</sup> bond [2.207(4) Å] and by the axial O–Sn–O and the equatorial C–Sn–C bond angles [160.1(2) and 124.8(4)°, respectively]. However, this type of dimethyltin coordination in POM chemistry is not unusual because it has been observed already in our 2D polymolybdate material [{(CH<sub>3</sub>)<sub>2</sub>Sn}<sub>4</sub>O<sub>2</sub>(MoO<sub>4</sub>)<sub>2</sub>].<sup>7</sup> Interestingly, this compound and **1a** were both synthesized at neutral pH.

The crystal packing of **1a** shows that the (W<sub>6</sub>O<sub>22</sub>)<sup>8-</sup> fragments are linked by *cis*-(CH<sub>3</sub>)<sub>2</sub>SnO<sub>3</sub> moieties, resulting in the 1D hybrid organic–inorganic POM assembly {**1**}<sub>∞</sub> (see Figure 3). Each hexatungstate fragment coordinates four (CH<sub>3</sub>)<sub>2</sub>Sn<sup>2+</sup> groups in such a way that two adjacent (W<sub>6</sub>O<sub>22</sub>)<sup>8-</sup> clusters are connected by two *cis*-(CH<sub>3</sub>)<sub>2</sub>SnO<sub>3</sub> moieties. Most likely, the polymeric **1a** starts to decompose in solution by rupture of the long Sn–O3S2<sup>ii</sup> bonds to give discrete molecular **1**. Almost certainly, the fifth position of the Sn coordination sphere in **1** is then occupied by a labile water molecule. This is reminiscent of the solution properties of our 2D material (CsNa<sub>2</sub>{[Sn(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>(β-XW<sub>9</sub>O<sub>33</sub>)}·7H<sub>2</sub>O)<sub>∞</sub> (X = As<sup>III</sup>, Sb<sup>III</sup>).<sup>6a</sup> Because of the flexible nature of the Sn center, a change to the tetrahedral coordination geometry is also not impossible but appears unlikely. We tried to perform solution <sup>183</sup>W and <sup>119</sup>Sn NMR experiments to ascertain this point, but the low solubility of **1a** did not allow us to obtain useful results.

The hybrid organic–inorganic chains in **1a** run parallel to the [101] direction (see Figure 3), with the [C(NH<sub>2</sub>)<sub>3</sub>]<sup>+</sup> cations and the water molecules arranged between the



**Figure 3.** Top: view of the crystal packing of **1a** along the crystallographic *b* axis (methyl H atoms, [C(NH<sub>2</sub>)<sub>3</sub>]<sup>+</sup> cations, and waters of hydration have been omitted for clarity). Bottom: details of the H-bond network viewed along the (101) direction.

(W<sub>6</sub>O<sub>22</sub>)<sup>8-</sup> fragments in bilayers parallel to the *ab* plane. In this way, a sequence of alternating hydrophobic (at *a* = 0, 1/2, and 1) and hydrophilic regions (at *a* = 1/4 and 3/4) is formed. The chains are held together by the [C(NH<sub>2</sub>)<sub>3</sub>]<sup>+</sup> cations through an extended and intricate network of strong N–H⋯O hydrogen bonds that are established between all NH<sub>2</sub> groups of [C(NH<sub>2</sub>)<sub>3</sub>]<sup>+</sup> and all terminal and bridging O atoms of (W<sub>6</sub>O<sub>22</sub>)<sup>8-</sup> that are not involved in coordination to Sn.

In summary, our work has shown that the (CH<sub>3</sub>)<sub>2</sub>Sn<sup>2+</sup> electrophile is also reactive toward WO<sub>4</sub><sup>2-</sup>, in addition to MoO<sub>4</sub><sup>2-</sup> and lacunary heteropolytungstates. This work has resulted in the first structurally characterized dimethyltin-containing isopolytungstate **1**. Polyanion **1** is composed of unprecedented (W<sub>6</sub>O<sub>22</sub>)<sup>8-</sup> clusters that are stabilized by two dimethyltin groups. Selective crystallization of **1** with guanidinium cations resulted in the solid-state 1D assembly **1a** via distorted trigonal-bipyramidal *cis*-(CH<sub>3</sub>)<sub>2</sub>SnO<sub>3</sub> moieties, providing another example of the unique linking and coordination ability of the dimethyltin electrophile. We plan to extend this work also to other organotin moieties in order to stabilize isopolyanion fragments not known to date.

**Acknowledgment.** S.R. thanks Gobierno Vasco/Eusko Jaurlaritz for his Postdoctoral Fellowship.

**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>.

IC0619862

(17) Fuchs, J.; Flindt, E. P. *Z. Naturforsch. B* **1979**, *34*, 412.

(18) (a) Maksimovskaya, R. I.; Burtseva, K. G. *Polyhedron* **1985**, *4*, 1559.

(b) Hastings, J. J.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1992**, 209.