

## Unprecedented Dinuclear Tin Derivative of Deprotonated $\beta$ -Cyclodextrins

Shun-Li Li, Ya-Qian Lan, Jian-Fang Ma,\* Jin Yang, Min Zhang, and Zhong-Min Su

Key Laboratory of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

Received January 16, 2008

Two unprecedented dinuclear tin compounds containing deprotonated  $\beta$ -cyclodextrins have been constructed by using different organotin and inorganotin precursors under solvothermal conditions, which display two dinuclear airscrew-like structures with different packing modes.

The field of organotin chemistry has been developed for 150 years.<sup>1</sup> Numerous organotin compounds have been prepared by the reaction of appropriate organotin precursors with carboxylic, phosphonic, and sulfonic acids, alcohols, and phenols.<sup>2,3</sup> The interaction of carbohydrates with organotin species has also been investigated. For example, it is found that the D-saccharose–Ar<sub>3</sub>Sn<sup>+</sup> conjugates are effective in marine antifouling paints.<sup>3,4</sup> A few crystal structures of the organotin complexes with partially protected sugars have been determined.<sup>3,5</sup> On the other hand, because the organotin complexes of unprotected sugars are presumed to be oligomeric, it is very difficult to obtain their crystals suitable for X-ray diffraction analysis.<sup>3,6</sup> As a special class of carbohydrates,<sup>7</sup> cyclodextrins have been generally used in the studies of molecular recognition, enzyme models, and molecular assemblies. It is also found that cyclodextrins can be used

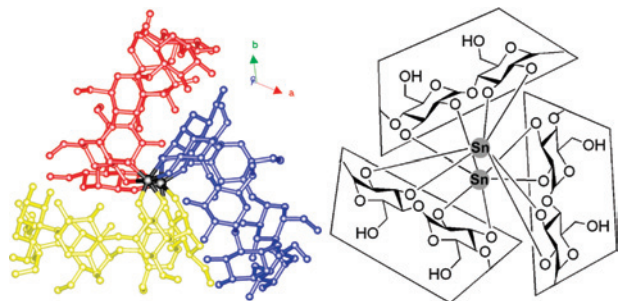
as multiply deprotonated polyolato ligands to form metal complexes in aqueous alkaline solutions.<sup>8</sup> An inclusion complex between allyldi-*n*-butyltin chloride and  $\beta$ -cyclodextrin has been reported.<sup>9</sup> It is supposed that the *n*-butyl or allyl group is inserted into the cavity of  $\beta$ -cyclodextrin, and no covalent Sn–O bonds are formed. No studies of true organotin complexes containing a covalent Sn–O bond between the Sn atom and deprotonated cyclodextrins have been reported. It is known that solvothermal methods can cause a reaction to shift from the kinetic to the thermodynamic domain and are optimal for crystal growth.<sup>10</sup> In a previous work,<sup>11</sup> a mixed-valence Sn–O cluster has been synthesized by using the solvothermal methods.

In this work, we intended to investigate the reaction between organotin precursors and cyclodextrins under solvothermal conditions. Fortunately, a novel dinuclear tin compound with the deprotonated  $\beta$ -cyclodextrins, [Sn<sup>IV</sup><sub>2</sub>( $\beta$ -CD)<sub>3</sub>]H<sub>8</sub>·H<sub>2</sub>O (**1**) (where  $\beta$ -CD is  $\beta$ -cyclodextrin), has been obtained<sup>12</sup> from the reaction of BuSnO(OH) and  $\beta$ -cyclodextrins. The result shows that the organotin precursor has translated into an inorganotin through Sn–C bond cleavage under the solvothermal condition. According to this result, we try to use SnCl<sub>4</sub>·5H<sub>2</sub>O as a raw material instead of an organotin precursor under the same reaction conditions, and compound [Sn<sup>IV</sup><sub>2</sub>( $\beta$ -CD)<sub>3</sub>]H<sub>8</sub> (**2**) has been synthesized successfully. It is interesting that compounds **1** and **2** display the first example of tin compounds based on deprotonated cyclodextrin by using solvothermal methods.

\* To whom correspondence should be addressed. E-mail: jianfangma@yahoo.com.cn.

- (1) (a) Frankland, E.; Ann, J. L. *Chemistry* **1849**, *71*, 171. (b) Frankland, E.; Ann, J. L. *Chemistry* **1853**, *85*, 329.
- (2) (a) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1. (b) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190. (c) Chandrasekhar, V.; Gopal, K.; Thilagar, P. *Acc. Chem. Res.* **2007**, *40*, 420.
- (3) Pellerito, L.; Nagy, L. *Coord. Chem. Rev.* **2002**, *224*, 111.
- (4) Smith, P.; Smith, L. *Chem. Ber.* **1975**, 208.
- (5) (a) David, S.; Pascard, C.; Cesario, M. *Nouv. J. Chim.* **1979**, *3*, 63. (b) Cameron, T. S.; Bakshi, P. K.; Thangarasa, R.; Gridley, T. B. *Can. J. Chem.* **1992**, *70*, 1623.
- (6) Nagy, L.; Gyurcsik, B.; Burger, K.; Yamashita, S.; Yamaguchi, T.; Wakita, H.; Nomura, M. *Inorg. Chim. Acta* **1995**, *230*, 105.
- (7) (a) D'Souza, V. T.; Lipkowitz, K. B. *Chem. Rev.* **1998**, *98*, 1741. (b) Szejtli, J. *Chem. Rev.* **1998**, *98*, 1743.
- (8) (a) Fuchs, R.; Habermann, N.; Klüfers, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 852. (b) Klüfers, P.; Schuhmacher, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1863. (c) Benner, K.; Ihringer, J.; Klüfers, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 5818. (d) Klüfers, P.; Piotrowski, H.; Uhlendorf, J. *Chem.—Eur. J.* **1997**, *3*, 601. (e) Geißelmann, A.; Klüfers, P.; Kropfgans, C.; Mayer, P.; Piotrowski, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 924.

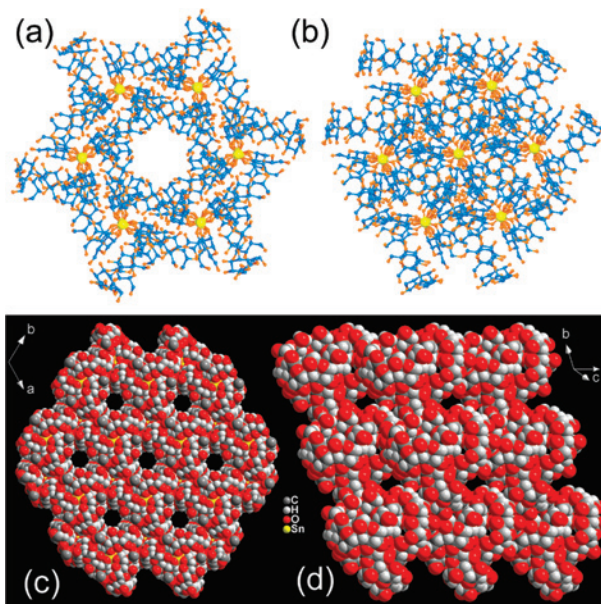
- (9) (a) Fornasier, R.; Marcuzzi, F.; Marton, D.; Favero, G.; Russo, U. *J. Organomet. Chem.* **2000**, *605*, 127. (b) Hapiot, F.; Tilloy, S.; Monflier, E. *Chem. Rev.* **2006**, *106*, 767.
- (10) (a) Babenau, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1026. (b) Wu, C. D.; Lu, C. Z.; Zhuang, H. H.; Huang, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 3836.
- (11) Zheng, G.-L.; Ma, J.-F.; Su, Z.-M.; Yan, L.-K.; Yang, J.; Li, Y.-Y.; Liu, J.-F. *Angew. Chem., Int. Ed.* **2004**, *43*, 2409.
- (12) Synthesis of compound **1**: A mixture of BuSnO(OH) (0.11 g, 0.50 mmol),  $\beta$ -cyclodextrin (0.56 g, 0.50 mmol), and NEt<sub>3</sub> (0.1 mL) in 15 mL of ethanol was heated in a Teflon-lined autoclave at 160 °C for 4 days. Upon cooling to room temperature, colorless crystals of compound **1** were collected. Yield: 38% yield (based on Sn). Synthesis of compound **2**: Compound **2** was prepared by a method similar to that of compound **1** by using SnCl<sub>4</sub>·5H<sub>2</sub>O (0.18 g, 0.50 mmol) instead of BuSnO(OH). Colorless crystals of compound **2** were collected with 35% yield (based on Sn).



**Figure 1.** Ball–stick representation of the structure of **1** (left). Schematic view of the structures of **1** and **2** (right).

Single-crystal X-ray structural analysis<sup>13</sup> reveals that the structure of compound **1** contains one kind of crystallographically unique cyclodextrin ion and two kinds of crystallographically unique Sn atoms that have the similar coordination environments. Each Sn ion is located on the genuine 3-fold rotation axis (Figure 1) and coordinated by six hydroxyl O atoms from three  $\beta$ -CD anions, showing a distorted octahedral geometry (Figure S1 in the Supporting Information). Each  $\beta$ -CD anion coordinates to two Sn ions through four hydroxyl O atoms, with 2<sup>A</sup>- and 3<sup>A</sup>-O atoms chelating one Sn ion and 2<sup>B</sup>- and 3<sup>B</sup>-O atoms chelating the other Sn ion (Figure S2 in the Supporting Information). The chelating coordination mode of the two glucose units in a  $\beta$ -CD anion is the same as that of the partially protected sugars in organotin complexes.<sup>3,5</sup> Three  $\beta$ -CD ions are bridged by two Sn ions with a Sn...Sn distance of 4.985 Å to form an airscrew-like structure of **1**, with three  $\beta$ -CD ions encircling the 3-fold axis where two Sn ions lie. Compound **2** shows a similar structure with a Sn...Sn distance of 5.061 Å.

Compounds **1** and **2** crystallize in  $P6_3$  and  $R3$  space groups, respectively, and show entirely different packing modes (parts a and b of Figure 2). As shown in Figure 2c, in the crystal structure of **1**, compound **1** stacks to form channels along the  $c$  axis. The space of the channel (approximately 6 Å  $\times$  6 Å) results from the packing of different molecules. The solvent-accessible volume occupies



**Figure 2.** (a and b) Ball–stick representations of the structures of **1** and **2** along the  $c$  axis. (c and d) Packing diagrams of **1** and **2** with channels along the different directions.

as much as 28.7% (2781.1 Å<sup>3</sup> per unit cell) of the crystal volume (9675.7 Å<sup>3</sup>).<sup>14</sup> The molecular packing of **2** generates the channels 5.0  $\times$  2.5 Å (Figure 2d). The solvent-accessible volume occupies as much as 32.5% (4796.0 Å<sup>3</sup> per unit cell) of the crystal volume (14 764.5 Å<sup>3</sup>). So, the density of compound **1** of 1.254 Mg m<sup>-3</sup> is larger than that of compound **2** (1.226 Mg m<sup>-3</sup>). The result indicates that compound **1** shows a closer packing than compound **2**. The complex molecules are linked by lattice–water molecules through hydrogen bonds, and a closer packing mode is formed.

In previous work, few structures of the metal complexes containing deprotonated cyclodextrins were isolated from the aqueous solution through a conventional reaction.<sup>8</sup> In comparison with the above-mentioned compounds, we have tried to use the solvothermal method to investigate the coordination chemistry of cyclodextrins. Compounds **1** and **2** exhibit novel structures, indicating that the solvothermal method is not only a versatile method in pursuit of multifunctional materials but also an effective route to synthesize novel tin compounds through the use of different organotin or inorganotin precursors. To the best of our knowledge, compounds **1** and **2** together constitute the first example of tin compounds based on deprotonated cyclodextrin by using solvothermal methods.

The X-ray photoelectron spectra of **1** and **2** show Sn 3d<sub>5/2</sub> peaks with binding energies of 485.3 and 485.8 eV, respectively (Figure S3 in the Supporting Information). The binding energies of tin are not very sensitive to the valence of tin, and the ranges of binding energies for different valences are overlapped. We cannot deduce the valence of tin in compounds **1** and **2** from this binding energy of 485.3 or 485.8 eV.

(13) (a) Single-crystal X-ray data of compounds **1** and **2** were collected on a Bruker Smart Apex CCD diffractometer at 293 K, with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710\ 73\ \text{\AA}$ ). The structure was solved with the direct method of *SHELXS-97*<sup>13c</sup> and refined with full-matrix least-squares techniques using the *SHELXL-97*<sup>13d</sup> program within WINGX.<sup>13e</sup> Non-H atoms were refined anisotropically. Selected bond lengths and bond angles are given in Table S1 in the Supporting Information. (b) Crystal data for **1**: hexagonal, space group  $P6_3$ ,  $M_r = 3652.27$ ,  $a = 20.300(19)\ \text{\AA}$ ,  $b = 20.300\ \text{\AA}$ ,  $c = 27.112(3)\ \text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$ ,  $V = 9675.7(13)\ \text{\AA}^3$ ,  $Z = 2$ ,  $\mu = 0.356\ \text{mm}^{-1}$ ,  $D_c = 1.254\ \text{Mg m}^{-3}$ ,  $F(000) = 3816$ ,  $T = 293(2)\ \text{K}$ , 61 355 reflections collected, 15 253 unique with  $R_{\text{int}} = 0.0476$ ,  $R1 = 0.0524$ ,  $wR2 = 0.1340$  [ $I > 2\sigma(I)$ ],  $\text{GOF} = 1.005$ . Crystal data for **2**: trigonal, space group  $R3$ ,  $M_r = 3634.26$ ,  $a = 19.9000(11)\ \text{\AA}$ ,  $b = 19.9000(11)\ \text{\AA}$ ,  $c = 43.051(1)\ \text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$ ,  $V = 14764.5(12)\ \text{\AA}^3$ ,  $Z = 3$ ,  $\mu = 0.350\ \text{mm}^{-1}$ ,  $D_c = 1.226\ \text{Mg m}^{-3}$ ,  $F(000) = 5694$ ,  $T = 293(2)\ \text{K}$ , 26 539 reflections collected, 12 748 unique with  $R_{\text{int}} = 0.0352$ ,  $R1 = 0.0595$ ,  $wR2 = 0.1472$  [ $I > 2\sigma(I)$ ],  $\text{GOF} = 1.016$ . The data were corrected for absorption by the multiscan. (c) Sheldrick, G. M. *SHELXS-97, A Program for Automatic Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997. (d) Sheldrick, G. M. *SHELXL-97, A Programs for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997. (e) Farrugia, L. J. *WINGX, A Windows Program for Crystal Structure Analysis*; University of Glasgow: Glasgow, U.K., 1988.

(14) The channel dimensions are estimated from the van der Waals radii for carbon (1.70 Å), nitrogen (1.55 Å), and oxygen (1.52 Å) in the analysis.

In order to obtain the atomic charges of tin in the complexes **1** and **2**, the model complexes were examined by natural population analyses (NPA) (see computational methods)<sup>15–18</sup> for **1** and **2** (Figure S4 in the Supporting Information). From the results, the natural charges of the endo Sn atoms are 2.616 and 2.647e for **1** and 2.609 and 2.658e for **2**, respectively. The natural atomic orbital occupancies of two Sn atoms are [core]5s(0.630)5p<sub>x</sub>(0.232)5p<sub>y</sub>(0.253)5p<sub>z</sub>(0.251) and [core]5s(0.630)5p<sub>x</sub>(0.230)5p<sub>y</sub>(0.239)5p<sub>z</sub>(0.236) for **1** and [core]5s(0.638)5p<sub>x</sub>(0.233)5p<sub>y</sub>(0.260)5p<sub>z</sub>(0.260) and [core]5s(0.628)5p<sub>x</sub>(0.236)5p<sub>y</sub>(0.239)5p<sub>z</sub>(0.240) for **2**, respectively. The atomic orbital occupancies of Sn atoms come from the covalent Sn–O component and oxygen's back-donation. The natural charges of the Sn atoms indicate that the valences of both Sn atoms are IV in **1** and **2**. To verify the results further, the +2e-, +4e-, -2e-, and -4e-charged complexes are calculated. The natural charges of two Sn atoms range

from 2.609 to 2.659e for **1** and from 2.612 to 2.662e for **2**, and their natural atomic orbital occupancies are almost consistent. These natural charges of tin in charged systems indicate that the atomic charges of tin in the complex will not change in such coordinated circumstances if the charge were introduced to cyclodextrin.

In conclusion, a pair of tin compounds containing deprotonated  $\beta$ -cyclodextrin has been isolated from the reactions of  $\beta$ -cyclodextrin and different tin precursors. This work shows the special importance of solvothermal methods for organotin chemistry and coordination chemistry of cyclodextrin. The solvothermal methods may provide an appropriate condition for Sn–C bond cleavage, and the Sn–C bond cleavage reaction can be used to prepare novel tin compounds.<sup>19</sup> A variety of novel tin compounds may be obtained under solvothermal conditions by changing ligands, tin precursors, solvents, and reaction temperatures. The studies of the solvothermal syntheses of novel tin compounds from organotin precursors are currently in progress in our laboratory.

**Acknowledgment.** We thank the National Natural Science Foundation of China (No. 20471014), Program for New Century Excellent Talents in Chinese University (NCET-05-0320), Program for Changjiang Scholars and Innovative Research Teams in Chinese University, the Science Foundation for Young Teachers of NENU (No. 20070309), and the Analysis and Testing Foundation of Northeast Normal University for support.

**Supporting Information Available:** Selected bond lengths and angles, XPS spectroscopic data, additional figures, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC8000784

- (15) Computational methods: All calculations were performed with the *Gaussian03* program package.<sup>16</sup> Density functional theory calculations were carried out with the three-parameter gradient-corrected exchange potential of Becke and the gradient-corrected correlation potential of Lee, Yang, and Parr (B3LYP)<sup>17</sup> with the LANL2DZ basis set. The atomic charges in the complex were calculated by NPA in NBO program.<sup>18</sup>
- (16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*, revision A.7; Gaussian Inc.: Pittsburgh, PA, 1998.
- (17) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (18) (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, version 3.1; University of Wisconsin:Madison, WI, 1990.

- (19) Chandrasekhar, V.; Gopal, K.; Sasikumar, P.; Thirumoorthi, R. *Coord. Chem. Rev.* **2005**, *249*, 1745.