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Synthesis, Structure, and H_2/CO_2 Adsorption in a Three-Dimensional 4-Connected Triorganotin Coordination Polymer with a sqc Topology

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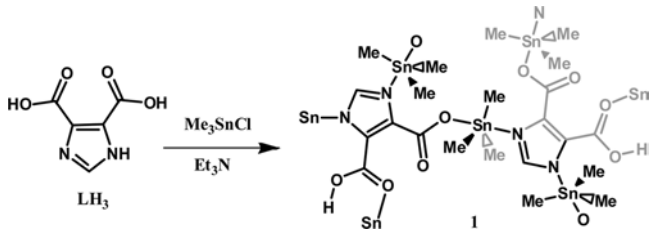
Supporting Information

ABSTRACT: A 4-connected triorganotin 3D coordination polymer in a sqc topology has been shown to possess 1D microchannels along its crystallographic *a* axis. This main-group-element-containing framework structure shows selective gas adsorption, preferring CO_2 and H_2 over N_2.

Organostannoxanes are an important family of main-group-element-containing organometallic compounds that have been attracting considerable interest in view of their enormous structural diversity.[1] In particular, the formation of organostannoxanes in the reactions of organotin oxides, hydroxides, and oxide hydroxides with protic acids have been investigated in great detail.[2] More recently, there have also been efforts to use organostannoxane platforms to support electroactive,[3] photoactive,[4] and multisite coordinating ligands.[5] Most of these investigations on the formation of organostannoxanes have been restricted to monofunctional protic acids [RCOOH, $R_2P(O)(OH)$, $RP(O)(OH)_2$, and RSO_3H]. Recently, the use of dicarboxylic acids and other difunctional reagents to assemble various types of metal−organic frameworks (MOFs), involving transition-metal ions or their complexes as nodes,[6] suggests that similar efforts on main-group elements should also be of interest. In this context, there have already been some studies from our laboratory and others on the reactions of dicarboxylic/disulfonic acids with organotin substrates that revealed the formation of compounds possessing extended structures.[7] However, none of these assemblies possess any applications such as gas storage or selective gas adsorption. Traditional porous solids such as zeolites/activated carbons do not seem to be very suitable for the separation of gases because of inappropriate pore sizes. MOFs, on the other hand, seem to offer more promise in this area; the separation and adsorption of gas molecules of different kinetic diameters have been demonstrated in recent literature.[8,9] One key structural feature that can accomplish the selective adsorption and separation of small gases is modulation of the pore size.[10,11] Interpenetrating networks, in general, and 4-connected networks, in particular, seem to be of potential interest in these applications.[12] In this connection, we report the synthesis and structural characterization of a 3-fold interpenetrating 3D coordination polymer that contains the trimethyltin motif as part of the repeat unit. We also report the selective gas adsorption (H_2 and CO_2) features of this novel main-group coordination polymer. Such a property is completely unprecedented, to the best of our knowledge, among organotin-containing coordination polymers.

The reaction of Me_3SnCl with imidazole-4,5-dicarboxylic acid in a 1:1 molar ratio afforded $[(Me_3Sn)_4(\mu\text{-}LH)_2]_n$ (**1**) Scheme 1. See also the Supporting Information (SI) for

Scheme 1



experimental details. Compound **1** crystallized in the chiral space group $P2_12_12_1$. The asymmetric unit contains four trimethyltin units connected to each other by two imidazole-4,5-dicarboxylate groups (LH^{2-}). Each of these ligands binds through the two imino nitrogen and two carboxylate oxygen atoms in a 4.1111 mode (Scheme1).[13] Each tin is pentacoordinate in a distorted trigonal-bipyramidal geometry (SI, Figures S1 and S2) containing an oxygen atom and a nitrogen atom in the apical positions [Sn3−O5, 2.425(4) Å; Sn3−N2, 2.310(5) Å].

The extended structure of **1** should have resulted in a 2D coordination polymer if the two ligands were in the same plane (SI, Scheme S1). However, because of rotation around the axial bonds around Sn3, the two LH^{2-} ligands are twisted with respect to each other with a dihedral angle of 53.7(2)° (SI, Figure S3a and Scheme S1) . This interesting structural feature results in the formation of a 3D coordination polymer (SI, Figure S3b). The crystal structure of **1** reveals a 3-fold parallel interpenetration to generate a uninodal (LH^{2-}) 4-connected

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sqc topology (according to a topological analysis carried out by using *TOPOS* software; Figure 1).[14] Owing to the 3-fold

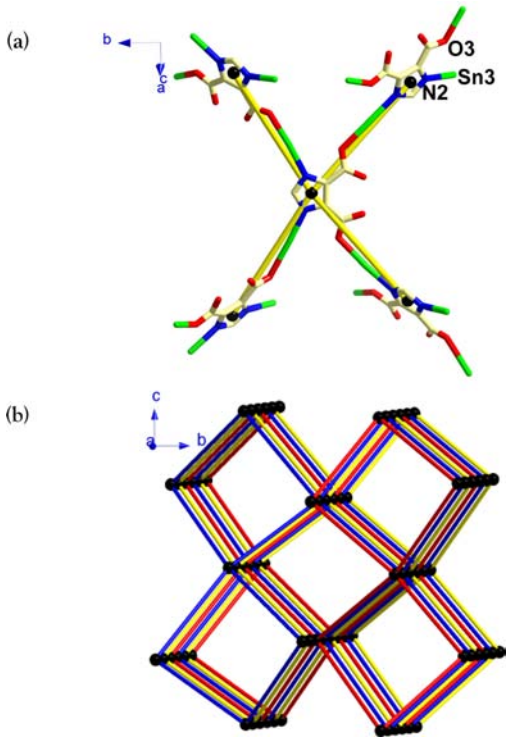

Figure 1. (a) 4-connected node represented by the ligand LH^{2-} (blue, N; green, Sn; red, O; black, dummy atom). (b) Representation of the 3-fold parallel interpenetrated 4c net of sqc topology [Schläfli symbol $(4^2.8^4)$].

parallel interpenetration, the open windows along the *b* and *c* axes present in the individual coordination polymer are closed in the crystal (Figure 2a). Because the interpenetration is

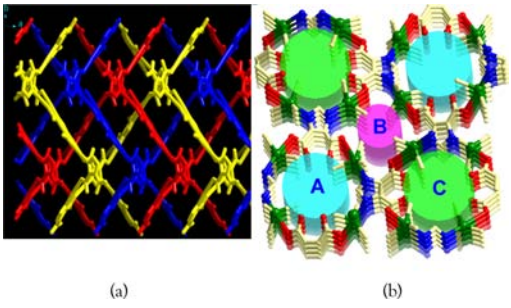

Figure 2. (a) View of the 3-fold interpenetration along the crystallographic *c* axis. (b) Microchannels A–C formed along the crystallographic *a* axis in the 3-fold interpenetrated 3D framework [A (~3.4 Å), B (~2.4 Å), and C (~3.3 Å); the values in parentheses are the effective pore sizes].

parallel along the crystallographic *a* axis, the three types of channels present in the individual polymer also remain intact in the single crystal. These three types of 1D channels (A–C) are decorated with methyl groups (connected to tin atoms), which reduces the effective aperture size (Figure 2b). However, the resultant effective size of the pores allows a size-dependent, selective gas adsorption property (vide infra). Thermogravimetric analysis (TGA) of **1** reveals that it is stable up to ~140 °C, after which it undergoes two consecutive weight losses at 141 and 260 °C. Finally at ~500 °C, the char residue is 10% (SI, Figure S6).

Compound **1** was nonporous to nitrogen because its highest aperture size (~3.4 Å) is smaller in comparison to the kinetic diameter of dinitrogen (N_2; 3.6 Å). So, it was not possible to determine the surface area from a nitrogen adsorption isotherm. However, **1** was able to take up hydrogen (H_2) and carbon dioxide (CO_2). The H_2 and CO_2 adsorption curves of **1** shown in Figure 3 reveal them to be reversible type-I

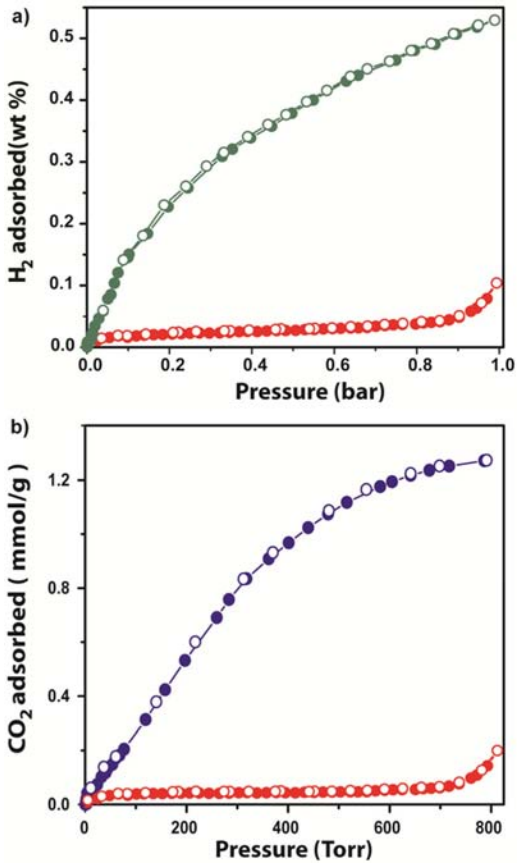

Figure 3. Selective gas adsorption isotherms of **1**: (a) H_2 (olive) and N_2 (red, circle) at 77 K; (b) CO_2 (blue) and N_2 (red) at 298K. The filled and open shapes represent adsorption and desorption, respectively.

adsorption isotherms at 77 and 298 K, respectively. Compound **1** shows a reversible H_2 sorption behavior, as shown in Figure 3a. H_2 (2.8 Å) uptake of **1** reached almost 0.54 wt % as the adsorbate pressure approached 1 atm at 77 K, which is comparable to those of some reported MOFs (SI, Table S2). As shown in Figure 3b, the framework exhibits a typical reversible CO_2 (3.4 Å) uptake profile at 298 K. The CO_2 uptake at 760 Torr is 1.27 mmol/g as the pressure approaches 1 atm. We have determined the surface area from a CO_2 adsorption isotherm (surface area 55.81 m^2/g). CO_2 uptake of **1** is comparable to previously reported MOFs (SI, Table S3).[15] It is important to mention that attractive materials for CO_2 uptake include those that may possess a moderate CO_2 adsorption but that show completely reversible isotherms.[16]

In conclusion, we have successfully synthesized a 3-fold parallel interpenetrated 3D coordination polymer **1** that contains trimethyltin motifs. **1** possesses three different methyl-decorated 1D channels along its crystallographic *a*

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axis; owing to the presence of such channels, this topological framework exhibits a gas sorption property. More importantly, because of the appropriate aperture size of its channels, **1** shows selective and *completely reversible* adsorption of both H_2 and CO_2 (in preference to N_2). This suggests the possible utility of **1** in applications involving gas separation. Further investigations are underway to unravel new synthetic routes that would allow for the assembly of novel layered and framework coordination polymers containing organotin motifs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information files (CIF) for **1**, some additional diamond figures, additional experimental data, and a thermogravimetric curve for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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