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Self-Assembly and Characterization of a Novel 2D Network Polymer Containing a 60-Membered Organotin Macrocycle

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The reaction of 1-(4-carboxyphenyl)-5-mercapto-1*H*-tetrazole with trimethyltin chloride in the presence of sodium ethoxide in benzene affords a novel 2D organotin network structure complex **1**, which is an unusual organotin network containing a hexanuclear 60-membered organotin macrocycle. The complex has been characterized by elemental analysis, IR, and ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy. Furthermore, we have also characterized the complex by X-ray crystallography.

Metal-directed self-assembly of organic ligands and metal ions or organometallic substances with various intriguing topologies has been extensively studied.[1,2] The increasing interest in this field is due to the potential relevance of such compounds in catalysis.[3] An important objective is also the synthesis of new higher soluble metal complexes useful for testing the distinctive reactivity patterns of the multimetallic systems. In recent years, organotin(IV) derivatives have received much attention, in both academic and applied research, because of the ability of the tin to afford stable bonds with carbons as well as with heteroatoms: a wide range of compounds found in organic synthesis and catalysis (synthesis of polyesters, polyurethanes, cross-linking of silicons, esterification, transesterification, polymerization, etc.) have been reported.[4] Especially, those carboxylate or mercapto ligands with additional donor atoms, such as a nitrogen atom, available for coordination to tin, have been revealed to help with the construction of interesting macrocyclic or multidimensional topologies.[5] In our previous work, we have reported several interesting organotin structures derived from mercaptocarboxylate ligands through self-assembly, such as six-tin-nuclear 32-membered macrocyclic complexes,[6] an eight-tin-nuclear macrocyclic complex with 2-mercapto-4-methyl-5-thiazoleacetic acid,[7] and a 3D framework with *meso*-2,3-dimercaptosuccinic acid.[8] To continue our research on the organotin(IV) complex in this field, we chose another fascinating ligand: 1-(4-carboxyphenyl)-5-mercapto-1*H*-tetrazole.

This ligand was chosen based on two considerations. First, both the carboxy and thiol groups in this ligand can form strong covalent bonds with the organotin moiety, thus providing sufficient thermodynamic stability for them to be stable in the solid state. Furthermore, this ligand has four additional heterocyclic nitrogen atoms, so it has a rich coordination chemistry and can help to construct multidimensional coordination polymers by acting as a multidimensional bridging linker. The above considerations stirred our interest in some detailed synthesis and structure patterns for triorganotin derivatives of the ligand. To our surprise, we obtained an unusual 2D network organotin complex **1** by use of 1-(4-carboxyphenyl)-5-mercapto-1*H*-tetrazole with trimethyltin chloride that consisted of a six-tin-nuclear 60-membered macrocycle. The complex has been characterized by elemental analysis, IR, and ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy. Furthermore, we have also characterized the complex by X-ray crystallography.[9]

The stretching frequencies of interest are those associated with the acid COO, Sn−S, Sn−O, and Sn−N groups. The strong absorption appearing at 429 cm^{-1} in the IR spectra of complex **1**, which is absent in the spectrum of the free ligand, is assigned to the Sn−O stretching mode of vibration.

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(9) Crystal data for **1**: M_r = 2738.98, 0.32 × 0.23 × 0.17 mm^3, triclinic, space group, $P\bar{1}$, a = 10.3659(16) Å, b = 16.232(2) Å, c = 20.607(3) Å, α = 104.210(3)°, β = 96.235(2)°, γ = 97.768(2)°, V = 3293.8(8) Å^3, Z = 1, D_{calc} = 1.381 mg/m^3, 10 525 independent reflections, $R1$ = 0.0942, wR2 = 0.2132, and S = 1.004 for observed reflections with $I < 2\sigma(I)$.

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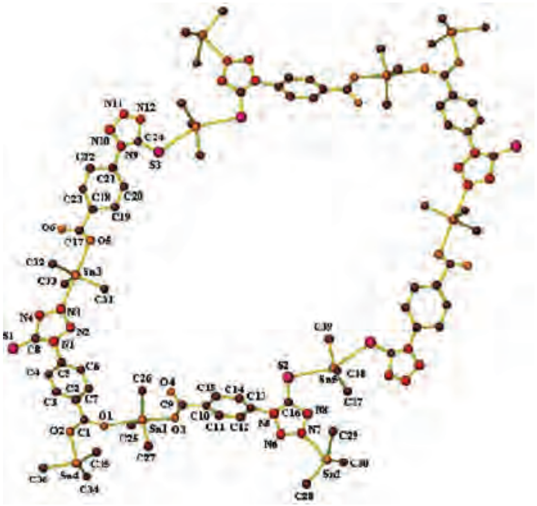

Figure 1. Repeating macrocycle unit of **1** (some atoms of the ligand groups are omitted for clarity).

Also, strong absorptions appearing at 1571 and 1426 cm^{-1} in the spectrum of complex **1** are assigned to the asymmetric and symmetric vibrations, respectively, of the COO moiety, while a medium-intensity band appearing at 476 cm^{-1} is assigned to the Sn−N stretching vibration. Furthermore, in the far-IR spectrum, a strong absorption appearing at 337 cm^{-1} is assigned to the Sn−S stretching mode of vibration. All of these values are consistent with those detected in a number of organotin(IV) derivatives.[10]

The ^{1}H NMR spectrum of complex **1** shows that the signals of the $-CO_2H$ and −SH protons in the spectrum of the ligand are absent in this complex, indicating the removal of the $-CO_2H$ and −SH protons and the formation of Sn−O and Sn−S bonds. The ^{13}C NMR spectrum of complex **1** shows a significant downfield shift of all carbon resonances compared with the free ligand; the shift is a consequence of an electron density transfer from the ligand to the metal atoms. The ^{119}Sn NMR spectrum of complex **1** exhibits four signals at −113.7, −117.2, −122.5, and −123.9 ppm, respectively, typical of five-coordinate species according to the literature,[11] which indicate the different sorts of coordinate entironments about tin atoms in complex **1**; these analyses are confirmed by the X-ray crystal structure of complex **1**.

The repeating macrocycle unit of complex **1** is shown in Figure 1; the width of the repeating macrocycle unit is 26.876 × 17.307 Å [transannular Sn(1)···Sn(1)#4 and Sn(3)···Sn(3)#3], which is larger than those of other organotin macrocycle complexes that we have reported.[6] By a search of CSD, we found that, even though a number of network organotin complexes have been studied before, such network structures containing a hexanuclear 60-membered macrocycle are rare. In complex **1**, all of the tin atoms are five-coordinated, and we can divide them into four sorts according to their different coordinated atoms. The two tin atoms [Sn(1) and Sn(4)] that are connected by two carboxyl oxygen atoms derived of adjacent ligands are regarded as sort I. The Sn(3) atom that is connected by one carboxyl oxygen atom and one heterocyclic nitrogen atom derived of adjacent ligands is regarded as sort II, the Sn(5) atom that is connected by two thiol sulfur atoms derived of adjacent ligands is regarded as sort III. and the Sn(2) atom that is connected by one heterocyclic nitrogen atom and one thiol sulfur atom is regarded as sort IV. All of the Sn−N, Sn−S, and Sn−O bond distances lie between the covalent bond length and the van der Waals radii of Sn−N, Sn−S, and Sn−O;[12] all of the tin atoms possess the distorted trigonal-bipyramidal geometry in complex **1**.

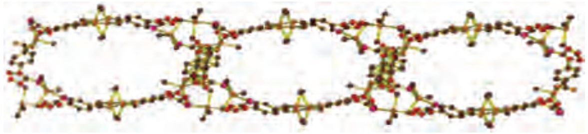

Figure 2. View of the 1D infinite chain structure with large cavities of complex **1** along the *a* axis (some of the ligand groups are disordered).

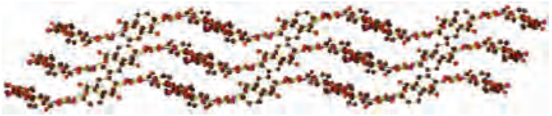

Figure 3. 2D network layer of complex **1**.

The repeating macrocycle units are linked by intermolecular Sn−N and Sn−S bonds, thus giving a 1D infinite chain (Figure 2); these infinite chains are further interlinked by intermolecular Sn−O bonds, forming a 2D macrocycle network layer with large cavities (Figure 3). The width of the large cavity can be evaluated by the transannular Sn···Sn distance, which is 23.699 × 10.697 Å. Although the dimensions of the cavities in this complex are large enough to capture some guest molecules, they in fact capture no guest molecules. This distinct structure is apparently different from the ionic complexes such as $\{[Mn(dcbp)]\cdot 2H_2O\}_n$ [dcbp = 4,4-dicarboxylate-2,2′-bipyridine][13] and $[Co(bix)_2(H_2O)_2][SO_4]\cdot 7\ H_2O$ [bix = 1,4-bis(imidazolylmethyl)benzene],[14] which all have substantially large pore apertures for guest molecules (constitute 18.2% and 27%, respectively) and reversibility of the "desorption−adsorption" process.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Date Centre as CCDC-664347. Copies of the data can be obtained free of charge upon application to the Director, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44-1223-336033; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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