Main-Group Clusters

A Mixed-Valence Tin–Oxygen Cluster Containing Six Peripheral Ferrocene Units**

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Although the multiferrocene compounds and tin–oxygen clusters are by now two well-developed areas,[1] syntheses of new multiferrocene compounds and tin–oxygen clusters will continue to be an attractive area of research. Many multiferrocene linear polymers and assemblies that contain ferrocene units in a cyclic arrangement have been synthesized by various methods.[1b,2] Among the multiferrocene compounds, dendrimers that contain a redox-active periphery of ferrocenes have been most actively investigated.[2a,3] Meanwhile many types of tin–oxygen clusters such as ladder,[4a] drum,[4b] cube,[4c] butterfly,[4d] cyclic trimer,[4e] single and double oxygen-capped,[5] doubly and triply bridged ladder[6] clusters have been prepared and characterized by X-ray diffraction. But until now very few multiferrocene compounds based on a tin–oxygen cluster are known.[7] Recently, Chandrasekhar et al. reported a multiferrocene compound that consists of six ferrocene units supported on a drumlike tin–oxygen cluster.[7] Thus, more novel multiferrocene compounds based on tin–oxygen clusters can be expected. Herein we report a new multiferrocene compound in which the six ferrocene units are held together by an unprecedented mixed-valence Sn^{II}_4–$Sn^{III}_4O_4$ cluster.

In this work, we intended to prepare new multiferrocene compounds based on tin–oxygen cluster by using solvothermal methods. The reaction of $n\mathrm{Bu_2SnO}$ with 1,1′-ferrocenedicarboxylic acid (H_2L) in a 1:1 stoichiometry in toluene was carried out in a teflon-lined autoclave at 180 °C for four days. The reaction proceeded with complete dealkylation of $n\mathrm{Bu_2SnO}$, and brown crystals of compound $Sn_8O_4L_6$ (**1**) were obtained [Eq. (1)].

$$n\mathrm{Bu_2SnO} + \mathrm{H_2L} \rightarrow \mathrm{Sn_8O_4L_6} \qquad (1)$$

The structure of compound **1** is shown in Figure 1.[8] The compound can be described as a tin–oxygen cluster connected to six ferrocene units. Unlike the previously reported multiferrocene compound,[3,7] the iron centers in compound **1** occupy the vertices of a regular octahedron. The core of the molecule is a Sn_8O_4 cluster (Figure 2). Four *endo* Sn atoms (Sn5, Sn6, Sn7, Sn8) and four μ_4-O atoms (O1, O2, O3, O4) occupy the corners of a distorted cube. Each face of this cube is defined by a four-membered $\{\overline{\text{Sn-O-Sn-O}}\}$ stannoxane ring. Furthermore, each μ_4-O atom is coordinated to one *exo* Sn atom (Sn1, Sn2, Sn3, Sn4) to form an Sn_8O_4 cluster. Each face of the cube is spanned by a 1,1′-ferrocenedicarboxylate ligand (Figure 3), and each *endo* Sn atom is bridged to one *exo* Sn atom through one μ_2-carboxylate group. The distances between opposite iron atoms are longer than 13 Å, which indicates that the molecule of compound **1** is nanosized and therefore can be isolated by nanomembrane filtration methods.[9] In the crystal structure of **1**, each *endo* Sn atom exhibits octahedral coordination geometry completed by three carboxylate O atoms and three μ_4-O atoms, whereas each *exo* Sn atom is coordinated by three carboxylate O atoms and one μ_4-O atom.

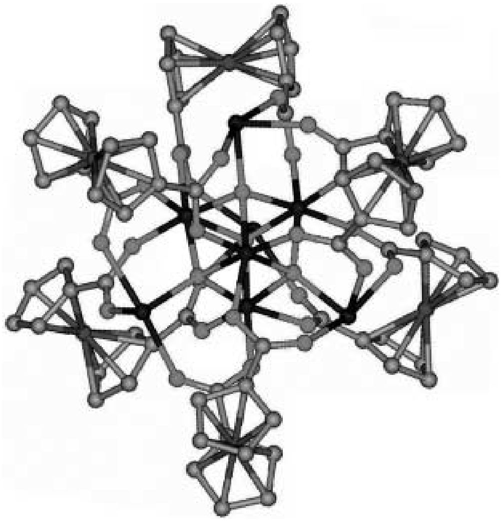

Figure 1. ViewerLite view of **1**. All hydrogen atoms are omitted for clarity.

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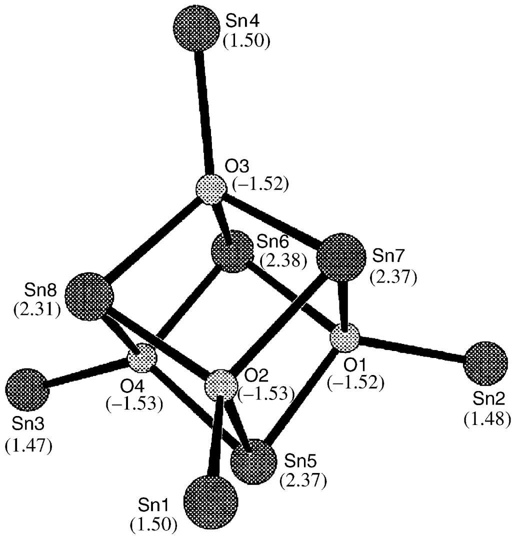

Figure 2. The framework of the tin–oxygen cluster. The values given in brackets are the natural charges of the atoms. Selected bond lengths [Å] and angles [°]: Sn1-O2 2.101(6), Sn2-O1 2.121(6), Sn3-O4 2.119(6), Sn4-O3 2.108(6), Sn5-O4 2.142(6), Sn5-O2 2.155(6), Sn5-O1 2.060(6), Sn6-O4 2.049(6), Sn6-O3 2.128(6), Sn6-O1 2.185(6), Sn7-O3 2.085(6), Sn7-O1 2.156(6), Sn7-O2 2.174(7), Sn8-O3 2.165(6), Sn8-O4 2.183(6), Sn8-O2 2.074(6); O1-Sn5-O4 82.4(2), O1-Sn5-O2 81.4(2), O4-Sn5-O2 80.6(2), O4-Sn6-O3 82.2(2), O4-Sn6-O1 81.6(2), O3-Sn6-O1 79.9(2), O3-Sn7-O1 81.5(2), O3-Sn7-O2 81.5(2), O1-Sn7-O2 78.9(2), O2-Sn8-O3 82.0(2), O2-Sn8-O4 81.5(2), O3-Sn8-O4 78.4(2), Sn5-O1-Sn6 96.2(3), Sn5-O1-Sn7 101.3(2), Sn6-O1-Sn7 96.7(2), Sn5-O2-Sn7 97.7(2), Sn5-O2-Sn8 99.9(2), Sn7-O2-Sn8 97.1(3), Sn6-O3-Sn7 100.7(3), Sn6-O3-Sn8 98.3(3), Sn7-O3-Sn8 97.1(2), Sn5-O4-Sn6 97.9(3), Sn5-O4-Sn8 96.9(2), Sn6-O4-Sn8 100.2(3).

Figure 3. The face of the cube spanned by a 1,1′-ferrocenedicarboxylate group.

In compound **1**, there are a total of twenty negative charges provided by twelve carboxylate ions and four oxide ions. These are balance by eight tin cations. Atomic charges of the compound were examined by natural bond-orbital (NBO) analysis (see Experimental Section). The natural charges of the tin–oxygen core are shown in Figure 2. The *endo* Sn atoms have the charges of 2.37 (Sn5), 2.38 (Sn6), 2.37 (Sn7), and 2.31 (Sn8), while the exo Sn atoms have the charges of 1.50 (Sn1), 1.48 (Sn2), 1.47 (Sn3), and 1.50 (Sn4). These values indicate that the valence for *endo* tin atoms is +3, and the valence for *exo* tin atoms is +2. The X-ray photoelectron spectroscopy (XPS) spectrum of **1**[10] shows an Sn 3d$_{5/2}$ peak with a binding energy of 486.7ev (Figure 4).[11] Commonly, Sn 3d$_{5/2}$ (not the Sn 3d$_{3/2}$ peak) is used to characterize the valence of tin. However, the binding energies of Sn^{II} and Sn^{III} are close to each other, and sometimes the Sn 3d$_{5/2}$ peaks of Sn^{II} and SN^{III} cannot be distinguished clearly. For the compound in this paper, Sn 3d$_{5/2}$ peak at 486.7 ev not only shows the presence of SnII but also shows the presence of Sn^{III}.

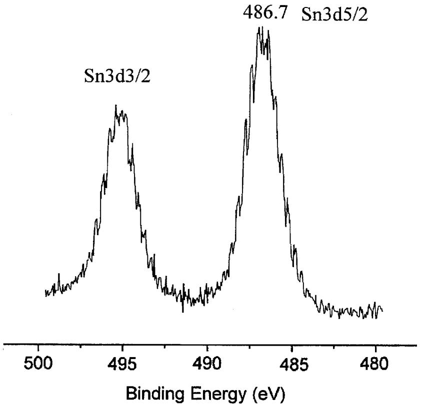

Figure 4. Tin-atom 3d emission peaks of the XPS spectrum for **1**.

The cyclic voltammogram of the compound **1** shows a quasireversible peak with an $E_{1/2}$ value of 0.44 V assigned to the uncoordinated ferrocenecarboxylate/ferroceniumdicarboxylate couple (Figure 5).[12,13] The other oxidation wave with an E value of 0.95 V indicates the tin–oxygen cluster is not stable and decomposes upon oxidation. Upon oxidation of the ferrocenyl group, the basicity of the dicarboxylate is decreased, and the group is susceptible to dissociation. This is different from the multiferrocene compound reported by Chandrasekhar et al., which does not decompose upon oxidation.[7a]

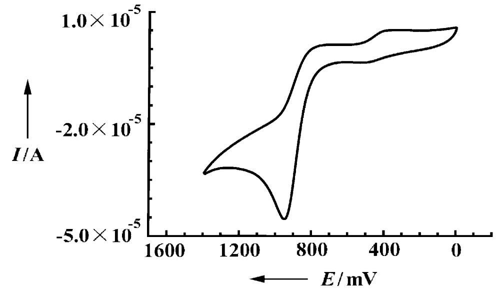

Figure 5. Cyclic voltammogram of **1** recorded at a scan rate of 0.1 Vs^{-1}.

In summary, a new multiferrocene compound based on a novel mixed-valence Sn^{II}_4–$Sn^{III}_4O_4$ tin–oxygen cluster has been synthesized and characterized. Further studies on synthesizing new multiferrocene compounds based on tin–oxygen clusters by using solvothermal methods are in progress.

Experimental Section

Synthesis of **1**: A mixture of nBu$_2$SnO (0.062 g, 0.25 mmol) and 1,1′-ferrocenedicarboxylic acid (0.069 g, 0.25 mmol) in 10 mL toluene was heated in a teflon-lined autoclave at 180 °C for 4 days. Upon cooling to room temperature, brown crystals of **1** were collected and washed with toluene. Yield: 60 % yield (based on nBu$_2$SnO). Elemental analysis (%) calcd for $C_{72}H_{48}Fe_6O_{28}Sn_8$ (**1**): C 32.69, H 1.83; found: C 32.53, H 1.74.

Computational methods: All calculations were performed with the Gaussian 98 program package.[14] Density functional theory (DFT) 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)[15] with the LANL2DZ basis set. The atomic charges in the complexes were examined by NBO analysis formulated in terms of natural atomic orbitals by using the NBO program.[16]

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Keywords: cluster compounds · cyclic voltammetry · cyclopentadienyl ligands · mixed-valent compounds · tin

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[8] Crystal data for $Sn_8O_4L_6$ **1**: Single-crystal X-ray diffraction data were recorded on a Rigaku RAXIS-RAPID image plate diffractometer by using the ω scan technique with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by using multiscan techniques.[17] The structure was solved by direct methods with SHELXS-97[18] and refined by full-matrix least squares with SHELXL-97[19] within WINGX.[20] All non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were refined as rigid groups. Crystal size $0.045 \times 0.339 \times 0.458$ mm^3, $T = 293(2)$ K, Monoclinic space group $C2/c$, $a = 34.364(7)$ Å, $b = 20.692(4)$ Å, $c = 25.114(5)$ Å, $V = 17857(6)$ Å^3, $Z = 8$, 70432 measured reflections, of which 19936 were unique ($R_{int} = 0.0407$); R values ($I > 2\sigma(I)$): $R1 = 0.0667$, $wR2 = 0.1971$, all data: $R1 = 0.1107$, $wR2 = 0.2131$, $-3.00 < \Delta\rho < 2.27$ e Å^{-3}. CCDC-220061 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[13] In cyclic voltammetry, electrochemical measurements were performed with a three-electrode cell at room temperature. A glassy carbon (GC) working electrode (3 mm in diameter) and a Pt-wire counter electrode were employed. The reference electrode was Ag/AgCl (saturated). Cyclic-voltammetry data were collected with LK98B Electrochemical Analyzer coupled to a HP-55 computer. Half-wave potentials were measured as the average of the cathodic and anodic peak potentials. The voltammogram was recorded in dimethyl formamide (DMF) that contained 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte and the potential was scanned from 0 to 1.5 V at scan rates 0.1 V s^{-1}.

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