Directed Formation of a Ferrocenyl-Decorated Organotin Sulfide Complex and Its Controlled Degradation

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S *Supporting Information*

ABSTRACT: Attachment of ferrocenyl (Fc) units to an organo-functionalized precursor yielded the Fc-decorated complex $[(R^{Fc}Sn)_4Sn_6S_{10}]$ [**1**; R^{Fc} = CMe$_2$CH$_2$C(Me)═N−N═C(Me)Fc], which shows different ligand dynamics in solution than in the solid state, as confirmed by NMR spectroscopy and by cyclic and differential pulse voltammetry. The addition of different amounts of hydrochloric acid to a solution of **1** produced the derivatives $[(R^{Fc}SnCl_2)_2S]$ (**2**) and $[R^{Fc}SnCl_3\cdot HCl]$ (**3**), the latter of which acts as a precursor to the formation/recovery of **2** or **1**, respectively.

Different types of organo-decorated main-group metal chalcogenide complexes have been investigated for many years because of their properties that derive from the combination of an inorganic (semi)metal chalcogenide core and an organic ligand shell.[1] Concerning group 14 chalcogenides, first studies were dedicated to syntheses and structures,[2,3] whereas recent developments focus more on the stabilities, functionalization, and resulting properties of the corresponding inorganic−organic complexes or networks.[4]

We have recently reported the synthesis and characterization of adamantane-type or double-decker-type (DD) $[(R^fT)_4S_6]$ or defect-heterocubane-type (SC) $[(R^fT)_3S_4]^q$ complexes [R^f = functional organic ligand like R^1 = C$_2$H$_4$COO(H) or R^2 = CMe$_2$CH$_2$C(Me)O; T = Ge or Sn; q = possible charge], which were prepared from precursors R^fTCl_3.[5] Complexes with R^2 are reactive toward hydrazine, as well as toward terminal hydrazine derivatives, hydrazones, or hydrazides.[5a,6,7] The DD-type thiostannate complex $[(R^2Sn)_4S_6]$ (**A**) undergoes a structural rearrangement upon reaction with terminal hydrazine derivatives, resulting in the formation of a double-SC (DSC) $[Sn_6S_{10}]$ topology, as in $[(R^4Sn)_4Sn_2S_{10}]$ [**B**; R^4 = CMe$_2$CH$_2$C(Me)═NNHPh].[5a,6] Aiming at a deeper understanding and control of the synthesis, reactivity, and physicochemical properties of organo-functionalized chalcogenide complexes, we currently concentrate on the attachment of new ligands to known complex topologies and study their directed degradation as well as interconversion between different forms.

The work has been extended by the introduction of ferrocenyl (Fc) ligands to study their influence on the structural and electrochemical properties of the decorated $[Sn_4S_6]$ complexes. Whereas the first experiments were undertaken with bis-substituted intramolecular (fC) linkers,[8] the current inves-tigations were undertaken with the monosubstituted Fc substituents presented herein (Scheme 1).

**Scheme 1. Synthesis of Compounds 1−3 by Stepwise Reactions Starting from Precursor Complex A**
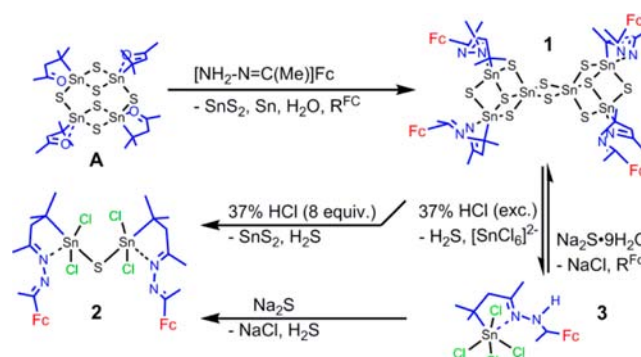
Derivatization of **A** with 4 equiv of H$_2$NN═C(Me)Fc was accompanied by rearrangement of the Sn/S core to form a DSC-type cage in $[(R^{Fc}Sn)_4Sn_2S_{10}]$ [**1**; R^{Fc} = CMe$_2$CH$_2$C(Me)═N−N═C(Me)Fc]. Previous studies of this rearrangement suggested that its occurrence or suppression is highly dependent on the steric demand of the ligand and its ability to form an intramolecular N → Sn coordination. Thus, the R^{Fc} ligand with a terminal Fc group seems to be bulky enough in this regard.

The treatment of **1** with 8 equiv of concentrated hydrochloric acid (37% HCl) yielded 2 equiv of the sulfide-bridged, dinuclear complex $[(R^{Fc}SnCl_2)_2S]$ (**2**) besides H$_2$S (4 equiv) and SnS$_2$ (2 equiv); by the addition of excess acid, the novel organotin chloride complex $[R^{Fc}SnCl_3\cdot HCl]$ (**3**) was obtained besides H$_2$S (10 equiv) and $[SnCl_6]^{2-}$ (2 equiv). The reaction of **3** with 2 equiv of Na$_2$S·9H$_2$O in a water/acetone mixture regenerated **1**, while the addition of anhydrous Na$_2$S in tetrahydrofuran (THF), however, led to the formation of **2** (Scheme 1). All three compounds were characterized by standard analytical techniques and single-crystal X-ray diffraction [see the Supporting Information (SI), Table S1].

The $[Sn_4S_6]$ core of the DD cage in **A** was rearranged during the reaction, yielding **1**, as observed in the case of **B**.[5a,6] In **1**, however, the $[Sn_6S_{10}]$ skeleton is connected to four Fc units via Schiff-base ligands (Figure 1). Two conformational isomers, **1a** and **1b**, were isolated upon two different reaction pathways at
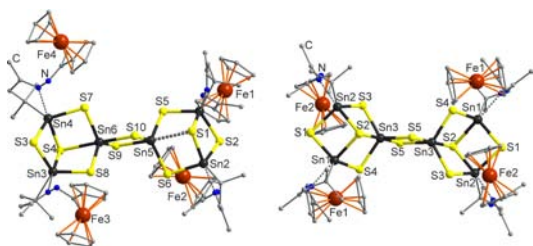
Figure 1. Molecular structures (without H atoms) of **1a** (left) and **1b** (right).

different crystallization conditions. Both crystallize in the space group $P\bar{1}$ but with different unit cells. Additionally, **1b** possesses molecular inversion symmetry, whereas **1a** exhibits no molecular symmetry.

Most of the bond lengths and angles within the $[Sn_6S_{10}]$ cores in **1a** and **1b** differ only marginally and agree with reported values (see the SI, Tables S2 and S3).[5a] The only notable exception is one unusually large Sn−S distance (Sn5···S1 3.007 Å) in **1a**, which is clearly associated with the solid state because ^{119}Sn NMR in solution produces only two signals (see the SI, Figure S12). This asymmetry of the Sn/S core in **1a** is accompanied by an asymmetric situation of the Fc-terminated ligands.

In the C_i-symmetric molecule of **1b**, the distances between the two Fe ions that belong to the same SC are naturally equal (Fe1···Fe2 6.1 Å), whereas for **1a**, this is obviously not the case. Here, two distances are observed (Fe1···Fe2 11.1 Å and Fe3···Fe4 6.3 Å), due to the different orientations of the Fc units, that are free to rotate about the C_{Cp}−C(Me) and/or N−N bonds of the Schiff-base ligand (see the SI, Scheme S1).

The different orientations of the Fc units in **1a** are obviously offset in solution, as confirmed by ^{1}H NMR spectra. Thus, the orientation of the Fc units in **1** seems to be highly flexible; the conformers realized in **1a** and **1b** are believed to be the result of the most effective packing of the molecules during crystallization, as indicated by intermolecular hydrogen-bonding interactions that can only be observed in the case of **1b** (see the SI, Figure S1).

The presence of four Fc units in close proximity to each other prompted us to investigate the electrochemical behavior of **1**. Cyclic and differential pulse voltammetry (CV and DPV) was performed in a CH_2Cl_2 solution in the presence of of tetra-*n*-butylammonium hexanfluorophosphate (TBFP; 0.1 M) at 25 °C (Figure 2). As shown in Figure 2, compound **1** undergoes two oxidation steps, which are almost overlapped in the CV ($E^1_{1/2}$ = 435 mV and $E^2_{1/2}$ = 615 mV at a scan rate of 100 mV/s) but sufficiently well separated in the DPV curve. The nearly equal intensities of the two peaks in the DPV graph suggest that each of
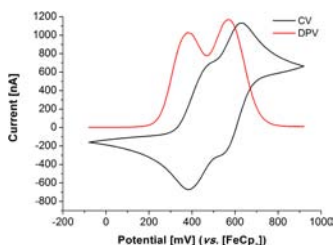

Figure 2. Cyclic and differential pulse voltammograms, recorded at a platinum electrode in a CH_2Cl_2 solution of **1** (1.61 mM), in the presence of TBFP (0.1 M). Scan ranges and rates: CV, −100 to +900 mV, 400 mV/s; DPV, −100 to +900 mV, 10 mV/s. Pulse amplitude 50 mV.

the two oxidations should involve the same number of (two) electrons.

The two-step oxidation of **1** indicates the existence of an electronic communication between the Fc units. According to previous investigations with multiple redox centers,[8,9] Fc units of different SC units are not likely to interact owing to the large Fe···Fe distance (**1a**, 13.0−14.5 Å; **1b**, 15.6−20.1 Å); they should thus behave identically. However, two vicinal Fc units that are located at the same SC moiety seem to communicate as a consequence of the flexibility of their relative orientations, as demonstrated in the different conformers (**1a** and **1b**). The comproportionation constant K_{comp}, which is a guide to the extent of electronic communication, was calculated on the basis of the separation between the formal electrode potentials of the two oxidation processes,[10] revealing that the electronic communication is relatively large (1.49×10^{12}) in spite of a small potential separation (see the SI, Table S7).

Electrospray ionization mass spectrometry in the positive ion mode, ESI-MS (+), of a methanolic solution of **1** not only exhibited the molecular peak of **1** (m/z 2325.63, $[M]^+$) but also provided deeper insight into the deconstruction or (re)assembly of Fc-ligated S/Sn cages in the gas phase. Three further species were identified, with the predominant peak according to $[(R^{Fc}Sn)_3S_4]^+$ (m/z 1452.96, $[M−R^{Fc}−3(SnS_2)]^+$); the composition belongs most probably to a SC-type fragment, which was also detected as the predominant peak in the positive-ion ESI-MS of **2**. Hence, this very stable structural motif forms from different sources under ESI-MS conditions. Compound **3**, in contrast, is unstable in the gas phase, exhibiting three decomposition products ($[HR^{Fc}SnCl_3]^+$, $[R^{Fc}SnCl_2]^+$, and $[R^{Fc}]^+$). The weak peak at m/z 1004.95 can be assigned to the oxo complex $[(R^{Fc}SnCl_2)_2O]^+$, which forms upon hydrolysis of **3** under ESI-MS conditions (see the SI, Figure S11).

Compound **2** crystallizes with two independent molecules in the asymmetric unit that exhibit nearly identical structural parameters (see the SI, Tables S4 and S5). An intermolecular Cl···H−C hydrogen bond (2.82 Å) interconnects the two molecules (see the SI, Figure S4). Depending on the chosen synthetic pathway, the asymmetric unit of **2** contains solvent molecules $\{[(R^{Fc}SnCl_2)_2S]\cdot3CHCl_3$ (**2a**); Figure 3, left} or
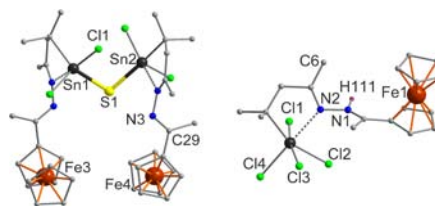
Figure 3. Molecular structures of **2a** (one of two independent molecules, left) and **3** (right). Solvent and H atoms (except the one labeled) are omitted for clarity.

cocrystallized with the byproduct $\{[(R^{Fc}SnCl_2)_2S]\cdot H_2S$ (**2b**)}. Compound **3** crystallizes in the orthorhombic space group $Pna2_1$, with four molecules in the unit cell (Figure 3, right).

The pentacoordinated Sn atoms retain their organometallic decoration during degradation by HCl addition in both compounds. In **2**, two of three $S^{2−}$ ligands per Sn atom in **1** were replaced by $Cl^−$ ligands, with one remaining S atom acting as a bridge to form the dinuclear complex. The addition of excess HCl, however, resulted in complete degradation by formation of the mononuclear complex **3**. Here, 1 equiv of HCl is caught

between two molecules through an intermolecular hydrogen bond Sn−Cl···H−N (see the SI, Figures S8 and S18), thereby converting the pentacoordinated Sn atom into a hexacoordinated one, similar to other organotin tri/tetrahalides with intramolecular coordination by a donor atom.[11]

The different reactions of **3** with Na_2S (see above) reflect the influence of the solvents: using the more polar water/acetone mixture, the reaction back to **1** was completed within a few minutes, with a distinct color change from purple via red to yellow; in THF, in contrast, the reaction stopped at an intermediate step (namely, upon formation of **2**), because the color of the suspension was still purple-red after stirring for 18 h.

We demonstrated the direct formation of a Fc-decorated organotin sulfide complex displaying electronic communication of vicinal Fc units, which can be split into di- or mononuclear organotin complexes by the addition of HCl. Future research is dedicated to the reactivity of the fragments toward chalcogenide compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray data (CIF), details of syntheses, analyses (IR, Raman, ESI-MS, ^1H, ^{13}C, and ^{119}Sn NMR, and EDX), and electrochemical measurements. Figures S1−S25, Scheme S1, and Tables S1−S10. 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.

■ ACKNOWLEDGMENTS

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