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A Methylated Oxo-Thio Stannate Cluster from a Non-Innocent Ionic Liquid

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Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday

Abstract. A new salt of the alkylated oxo-thio stannate cluster $[Sn_{10}O_4S_{16}(SMe)_4]^{4-}$, $(C_4C_4C_1Im)_4[Sn_{10}O_4S_{16}(SMe)_4]$ (**1**), was obtained by ionothermal treatment of $K_4[SnS_4]\cdot4H_2O$. The reaction was carried out in the ionic liquid 1,3-dibutyl-2-methylimidazolium chloride, $(C_4C_4C_1Im)Cl$, which proved to be non-innocent against the chalcogenido metallate species in the reaction mixture. In continuation of our first studies on alkylation of very weakly nucleophilic chalco-genido metalate anions, this study served to prove that an N-bonded alkyl group is selectively released from the imidazolium cation of the ionic liquid, and it served to show that methylation is favored over butylation. The title compound is one of the rare cases, in which the cations of the salt, which stem from the ionic liquid, could be crystallographically determined without problems.
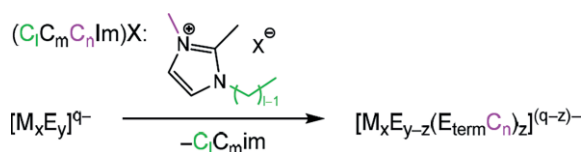
Introduction

The investigation of nano-sized metal chalcogenide compounds is a very topical field of inorganic and materials chemistry,[1–4] owing to corresponding properties that range from uncommon structural[5–8] and opto-electronic[9–12] properties to specific reactivities.[13,14] Of particular interest with regard to ecological and economical aspects are mild preparation conditions and controlled post-synthetic treatment.[15,16]

Recently, we reported about a benign methylation method by application of ionothermal synthesis conditions, which at the same time turned out to be suitable for very weak nucleophiles, such as chalcogenido metalate anions. Notably, while all conventional alkylation procedures have failed in the methylation of such anions to date, the ionothermal treatment in an imidazolium-based ionic liquid allowed for selective post-synthetic methylation of the terminal chalcogenide ligands of several different chalcogenido metalate clusters (Scheme 1).[17]

Notably, an inverse reactivity of ionic liquids was previously observed for large Ga/Cu/S clusters, where the neutral imidazole acted as coordinating ligands to a Ga atom upon release of one alkyl group.[5]

As the application of this uncommon methylation method may be very beneficial in synthetic chemistry given the rela-

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Scheme 1. General synthesis scheme for the alkylation of chalcogenido metalate units by ionothermal reactions in $(C_lC_mC_nIm)X$ (X = Cl, $[BF_4]$). Indices l, m, and n denote the number of carbon atoms of the alkyl substituents at the N atoms (l, green; n, pink) and the C atom in between (m, black) of the imidazolium ring. The neutral imidazole is denoted as C_lC_mim here.

tively low toxicity of ionic liquids, we are currently about to expand and generalize the method, and we also try to understand the ongoing processes, which are by no means trivial.

In the course of these studies, we were interested in the origin of the transferred alkyl groups. For this, we used the ionic liquid $(C_4C_4C_1Im)Cl$ (**A**),[18] possessing another substitution pattern than the previously used $(C_4C_1C_1Im)Cl$. This also served to prove the selectivity for the transfer of methyl groups over butyl groups.

Herein, we report on the formation of a new salt of the methylated oxo-thio stannate cluster anion $[Sn_{10}O_4S_{16}(SMe)_4]^{4-}$ by this method, $(C_4C_4C_1Im)_4[Sn_{10}O_4S_{16}(SMe)_4]$ (**1**), which allowed to address the issues mentioned above.

Notably, in compound **1** all cations could be determined by single-crystal X-ray diffraction, as this fortunately is a rare case without heavy disorder of the cation substructure.

Results and Discussion

$(C_4C_4C_1Im)_4[Sn_{10}O_4S_{16}(SMe)_4]$ (**1**) was synthesized by ionothermal treatment of $K_4[SnS_4]\cdot4H_2O$ in $(C_4C_4C_1Im)Cl$, as illustrated in Scheme 2.

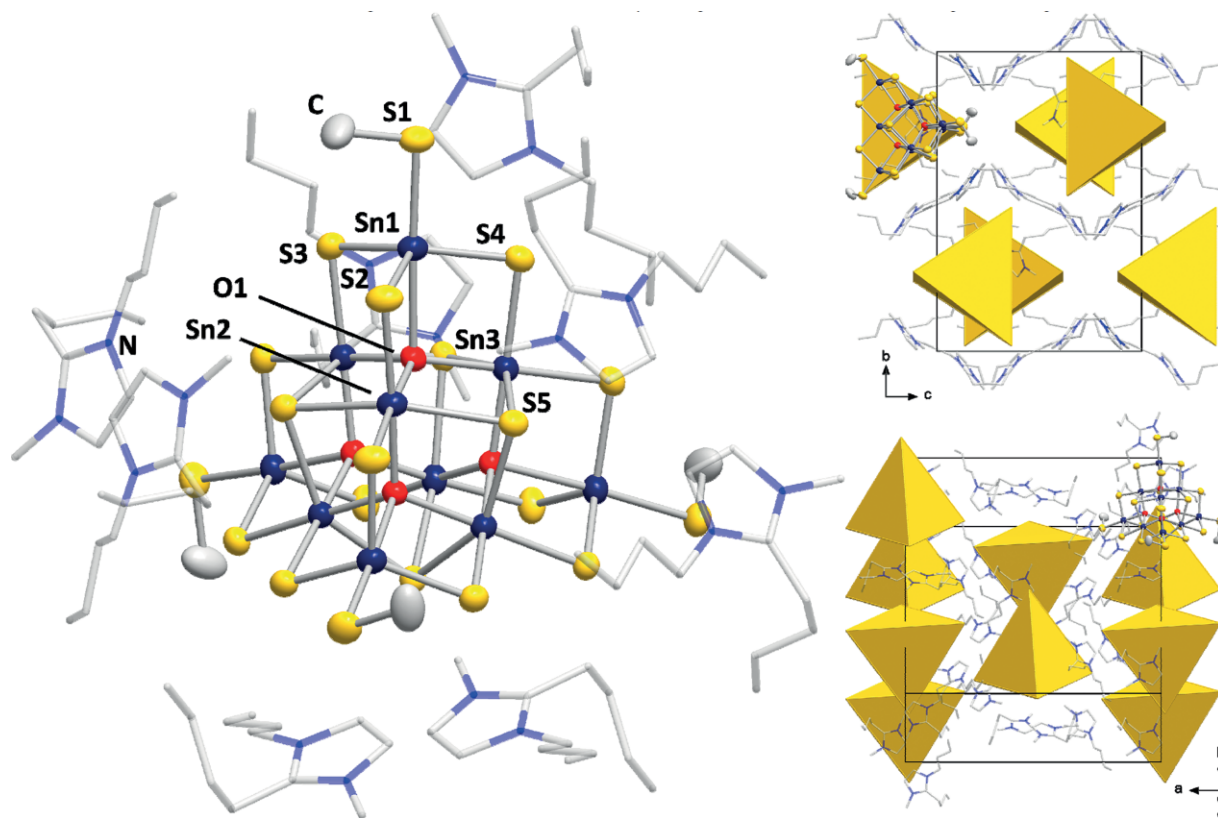**Figure 1**. (a) Molecular structure of the methylated cluster anion $[Sn_{10}S_{16}O_4(SMe)_4]^{4-}$ and the surrounding $(C_4C_4C_1Im)^+$ cations. (b) View of the (extended) unit cell of **1** along the crystallographic *a* axis. (c) View of the (extended) unit cell of **1**, approximately along <0,–1,–1>. In (b) and (c), $[Sn_{10}S_{16}O_4(SMe)_4]^{4-}$ clusters are shown as yellow tetrahedra. Ellipsoides are drawn at the 50 % probability level. For clarity, hydrogen atoms are omitted and cations are drawn as semi-transparent wires.

$$K_4[SnS_4]\cdot 4H_2O \xrightarrow[\substack{DMMP \\ 120\,°C,\ 4d}]{(C_4C_4C_1Im)Cl} (C_4C_4C_1Im)_4[Sn_{10}O_4S_{16}(SMe)_4]$$
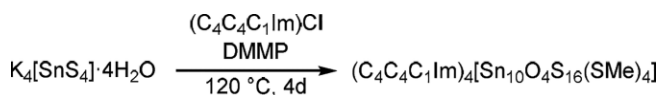
Scheme 2. Synthesis of $(C_4C_4C_1Im)_4[Sn_{10}O_4S_{16}(SMe)_4]$ (**1**). DMMP denotes 2,6-dimethylmorpholine.

The $(C_4C_4C_1Im)^+$ cation possesses two butyl groups, one at N1 and one at C1, while one methyl group is bonded to N2. Hence the observation of a methylated cluster is a clear prove for (1) the transfer of an N-bonded alkyl substituent, and (2) the selectivity for a methyl transfer instead of a butyl transfer.

Compound **1** crystallizes as colorless blocks in the tetragonal crystal system, space group $I4_1/a$, with four formula units within the unit cell. The compound consists of the known methylated cluster core $[Sn_{10}S_{16}O_4(SMe)_4]^{4-}$,[17] while four $(C_4C_4C_1Im)^+$ cations act as counterions. The cluster structure and its embedding into the counterion environment is shown in Figure 1a, two views of the packing of cations and anions are given in Figure 1b and c.

The anion is based on a (neutral) T3 supertetrahedron of the (hypothetical) composition "$[Sn_{10}S_{20}]$". Four O^{2-} anions are incorporated in this framework, thereby forming an inner "*anti*-T2" supertetrahedron of four O and ten Sn atoms. The four terminal sulfide ligands of the inorganic $[Sn_{10}S_{20}O_4]^{8-}$ cluster core bind one methyl group each to form the $[Sn_{10}S_{16}O_4(SMe)_4]^{4-}$ anion in **1**.

In the crystal structure of **1**, the methyl C atoms at the terminal sulfide ligands of the cluster and those of the charge-balancing $(C_4C_4C_1Im)^+$ counterions could be localized on the difference Fourier map. The counterions are situated above the faces of the supertetrahedral anions, and in this way separate them from each other in a spatially efficient way. In comparison to the $(C_4C_1C_1Im)^+$ cation used in former experiments, the additional butyl substituent increases the flexibility of the cation. However, instead of causing even heavier disorder, the flexibility is apparently used to adopt perfectly to the shape of the cluster.

The interatomic distances within the cluster core are characteristic for a cluster that bears methyl groups at the terminal sulfide ligands: The distance between the four "outer" Sn1 atoms, which bind to the terminal S1 ligands, and the O1 atoms is 2.461(3) Å. The six "inner" Sn atoms (Sn2/Sn3) form Sn–O bonds with a length of 2.091(3)–2.110(3) Å. The Sn–(μ-S) bonds vary between 2.3957(15) and 2.4715(15) Å, while the Sn–(μ₃-S) bond lengths exhibit values in the range 2.5942(13)–2.6327(12) Å. The most characteristic bond is Sn–S_{term}, hence between Sn1 and S1, as its length allows to discriminate between an unsubstituted terminal S atoms, such as in the purely inorganic anion $[Sn_{10}O_4S_{20}]^{8-}$,[19] and a terminal SR group (R = alkyl substituent). In **1**, the Sn–S_{term} distance amounts to 2.4365(15) Å. All values are in perfect agreement with the ones reported for related salts.[17] This can addition-

ally be taken as an indirect proof of the alkylation of clusters in cases where the methyl group could not be crystallographically determined.

The view of the packing of ions in the crystal structure of **1** indicates a wave-like arrangement of the cations between the anions (Figure 1b), extending parallel to the *c* axis. In addition to ionic interactions, the cations and anions in **1** undergo H bonding interaction (see Figure S1, Supporting Information). Nearest contacts between S atoms of the anionic cluster and H atoms of the imidazolium cations are 2.7262(15)– 3.2179(14) Å. Moreover, each cluster anion is connected to four adjacent cluster anions via two S···H(–C) interactions each per terminal S–CH$_3$ group [3.0142(15) Å].

To confirm the presence of S–Me groups in the bulk material, we recorded an SC-Raman spectrum of **1**, which is shown in Figure 2. Characteristic bands of the S–C$_{Me}$ vibration can be found at 700 cm^{-1}, the signal of the C$_{Me}$–H vibration is located around 1500 cm^{-1} (Figure 2a). As shown in Figure 2b, the signal groups between 150 and 400 cm^{-1}, which are assigned to the vibrations of the cluster core, match the cluster vibrations reported recently.[17] Hence, the presence of (C$_4$C$_1$C$_1$Im)$^+$ instead of (C$_4$C$_1$C$_1$Im)$^+$ cations, i.e., the presence of another butyl group instead of a methyl group, does not affect the bonding within the supertetrahedral anions. The signal group of the imidazolium C–H vibrations at around

2900 cm^{-1} (Figure 2c) is nearly the same as reported, which was expected as the imidazolium substituents differ in their ratio only, but not in their nature. The Raman spectrum thus confirms the situation found in the crystal structure.

Conclusions

By application of (C$_4$C$_4$C$_1$Im)Cl instead of (C$_4$C$_1$C$_1$Im)Cl as reaction medium of the ionothermal synthesis of the methylated oxo-thio stannate cluster [Sn$_{10}$O$_4$S$_{16}$(SMe)$_4$]$^{4-}$, we were able to prove that the methylation of these weakly nucleophilic chalcogenido metalate clusters by non-innocent ionic liquids involves the alkyl groups at an imidazolium N atom. We further learned from this study that a methylation is strongly preferred over a butylation, as both organic groups would have been available on imidazolium N atoms in principle. In future work, we are going to systematically expand the application of this method to the controlled alkylation of such compounds, also with other organic groups, by corresponding design of the imidazolium cation.

Experimental Section

General: All manipulations were performed in a dry argon atmosphere using standard Schlenk or glovebox techniques. Elements were used as received: K lumps (Acros Organics, 98%), Sn powder (Sigma–Aldrich, 99%), and S powder (Alpha Aesar, 99,999%). 2,6-Dimethylmorpholine (DMMP; 97%; Acros Organics) was distilled from CaH$_2$ and stored over molecular sieves (3 Å). 1-Butyl-2,3-dimethylimidazolium chloride, (C$_4$C$_1$C$_1$Im)Cl, was synthesized according to the literature.[18] The starting material K$_4$[SnS$_4$]·4H$_2$O was prepared by solid state reaction of K$_2$S, Sn and S according to the literature.[20] The raw product was purified by water-extraction.

Synthesis of (C$_4$C$_4$C$_1$Im)$_4$[Sn$_{10}$O$_4$S$_{16}$(SMe)$_4$] (1): 50 mg of K$_4$[SnS$_4$]·4H$_2$O (0.11 mmol), 500 mg of (C$_4$C$_4$C$_1$Im)Cl, and 100 μL of DMMP were sealed in a duran glass ampoule, heated to 180 °C and kept at this temperature for four days. The mixture was then allowed to cool down to room temperature. Colorless crystals of **1** were obtained as colorless blocks in approximately 22% yield.

X-ray Diffraction: X-ray data were collected with a Stoe IPDS2 diffractometer using Mo-K_α radiation (λ = 0.71073 Å; T = 100 K) equipped with an Oxford Cryosystems module. Structure solution by dual space methods and full-matrix least-squares refinement against F^2 were carried out using using SHELXT15, SHELXL15, and OLEX2 software.[21] The non-hydrogen atoms were anisotropically refined.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1980642 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Raman Spectroscopy: Raman data were collected on an S&I MonoVista CRS+ device. The measurements were performed with a laser wavelength of 532 nm and a grating of 300 grooves per mm. The measurement had duration of 5 s and 10 coadditions.

Supporting Information (see footnote on the first page of this article): Further details on crystallographic data and Raman spectra.
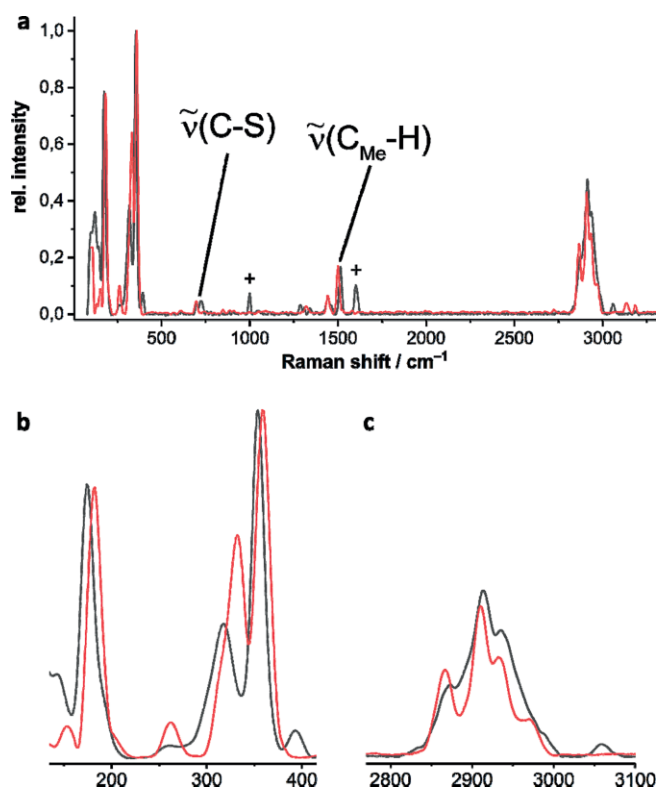

Figure 2. Raman spectra of (C$_4$C$_4$C$_1$Im)$_4$[Sn$_{10}$S$_{16}$O$_4$(SMe)$_4$] (**1**, red) and (C$_4$C$_1$C$_1$Im)$_4$[Sn$_{10}$S$_{16}$O$_4$(SMe)$_4$] (black). Signals of the immersion oil are denoted by "+". (a) Overview spectrum indicating bands of the S–C$_{Me}$ vibrations around 700 cm^{-1} and bands of the C$_{Me}$–H vibrations around 1500 cm^{-1}. (b) Characteristic bands representing vibrational modes of the cluster core. (c) Characteristic bands representing the C$_{Im}$–H vibrations.

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