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$Sn_3I_8 \cdot 2$(18-crown-6): a Mixed-Valent Tin-Crown-Ether Complex

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By reaction of SnI_2, SnI_4, and crown ether (18-crown-6) in the ionic liquid $[NMe(n\text{-}Bu)_3][N(Tf)_2]$, $Sn_3I_8 \cdot 2$(18-crown-6) is obtained in the form of black, plate-shaped crystals and crystallizes with a monoclinic lattice symmetry. In detail, $Sn_3I_8 \cdot 2$(18-crown-6) is constituted of trigonal-bipyramidal $[SnI_5]^-$-anions and $[Sn_2I_3(\text{18-crown-6})_2]^+$-cations. The cation exhibits an endocyclical coordination of Sn^{2+} by the crown ether. Both constituents are linked via long-ranging I−I contacts to form an infinite network. Besides crystal structure analysis, the mixed valence state of tin is evidenced by ^{119}Sn-Mössbauer spectroscopy.

Introduction

Iodometallates of the main group 13, 14, and 15 metals are of general relevance with regard to their semiconductor-type electrical and optical properties.[1,2] This includes applicational issues such as photovoltaics,[3] thermoelectrics,[4] and high-power batteries.[5] To this concern, especially iodostannates have gained substantial interest.[6,7] From the fundamental science perspective, the chemistry of tin halides is dominated by compounds containing either divalent or tetravalent tin. Very few examples are known to contain Sn(III).[8,9] Knowledge on mixed-valent tin halides is rather limited, too. Namely, this includes the binary compounds Sn_2S_3 and Sn_2F_6,[10,11] cluster-type metal-organic compounds such as $Sn(II)_2Sn(IV)_2F_4(O_2CCF_3)_8 \cdot 2CF_3CO_2H$ or $[Sn(\mu_3\text{-}NSnMe_3)]_4$,[12,13] as well as the organic-based perovskite $[H_3N(CH_2)_7NH_3]_8(CH_3NH_3)_2Sn(IV)Sn(II)_{12}I_{46}$.[14] These mixed-valent iodostannates typically exhibit low-dimensional structural building units and band-gap structures that have already turned out to be promising towards the above mentioned applications.

As a part of our studies regarding the potential benefit of ionic liquids in inorganic synthesis,[15,16] $Sn_3I_8 \cdot 2$(18-crown-6) is gained as a novel mixed-valent tin compound. Herein, ionic liquid was used as a polar but aprotic liquid-phase to guarantee a sufficient diffusion even at comparably low temperatures.[17] According to X-ray structure analysis the iodostannate is constituted of individual $[SnI_5]^-$-anions and $[Sn_2I_3(\text{18-crown-6})_2]^+$-cations. The presence of Sn(II) and Sn(IV) is evidenced by ^{119}Sn-Mössbauer spectroscopy.

Experimental Section

All experimental and analytical studies were performed with argon as inert-gas atmosphere (i.e., Schlenk techniques or glove-boxes). The commercially available starting materials SnI_4 (≥ 99.999 %, Sigma-Aldrich), SnI_2 (≥ 99.999 %, Sigma-Aldrich), and

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Table 1. Crystallographic data of $Sn_3I_8\cdot 2$(18-crown-6)

formula	$C_{24}H_{48}O_{12}Sn_3I_8$
crystal system/space group	monoclinic / $P2/n$ (No. 13)
cell parameters	$a = 12.418(3)$ Å $b = 7.911(2)$ Å $c = 24.586(4)$ Å $\beta = 92.03(3)°$ $V = 2414.9(2)$ Å^3
formula per unit cell	$Z = 2$
calculated density	$\rho_{calc} = 2.61$ g cm^{-3}
temperature	$T = 203$ K
measurement device	imaging plate diffraction system (IPDS I, STOE)
radiation	graphite-monochromated Mo K_α ($\lambda = 0.71073$ Å)
measurement limits	$3.3° \leq 2\theta \leq 52.1°$ $-15 \leq h \leq 15$, $-9 \leq k \leq 9$, $-30 \leq l \leq 29$
crystal size	$0.16 \times 0.13 \times 0.09$ mm
absorption coefficient	$\mu = 6.7$ mm^{-1}
absorption correction	numerical (T_min = 0.192, T_max = 0.323)
no. of reflections	18916 measured, 4628 independent
data averaging	$R_{int} = 0.056(1)$
structure refinement	full matrix least-squares on F_o^2; anisotropic displacement parameters for all non-hydrogen atoms
no. of parameters	216
residual electron density	1.57 to −1.22 e/Å^3
figures of merit	$R1 = 0.038$ $R1$ (3834 $F_o^2 > 4\sigma(F_o^2)$) = 0.027 $wR2 = 0.060$ GoF = 1.027

Table 2. Selected Bond Lengths and Angles of $Sn_3I_8\cdot 2$(18-crown-6) in Comparison to SnI_2 and SnI_4[a]

bond lengths/pm		bond angles/deg	
Sn1−I1	287.2(1)	I_{ax}−Sn2−I_{ax}	178.1(1)
Sn1−I2	355.2(1)	I_{ax}−Sn2−I_{eq}	89.1(1)−90.5(1)
Sn2−I	273.0(1)−287.3(1)	I_{eq}−Sn2−I_{eq}	119.4(1)−120.3(1)
Sn1−O	261.2(1)−293.7(1)	Sn1−I2−Sn1	142.1(1)
I−I	406.0(1)−409.4(1)	I2−Sn1−I1	165.3(1)
		O−Sn1−O	167.3(1)−175.5(1)
Sn−I (SnI_4)[20]	263.0		
Sn−I (SnI_2)[19]	300.4−325.1		

[a] ax: axial, eq: equatorial.

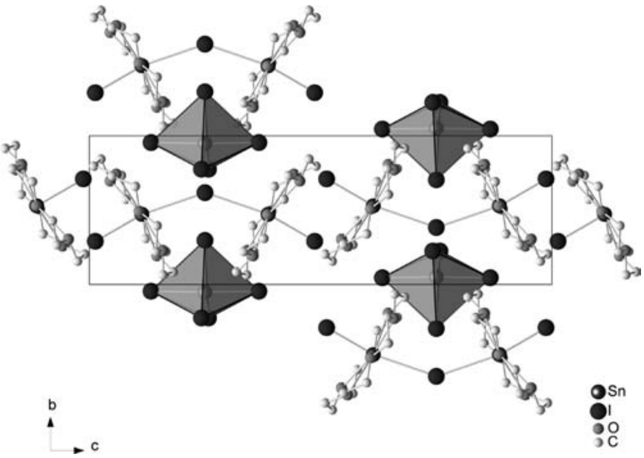

Figure 1. Unit cell of $Sn_3I_8\cdot 2$(18-crown-6).

18-crown-6 (≥ 99 %, Acros) were used subsequent to overnight drying in vacuum. The synthesis of the ionic liquid [NMeBu$_3$][N(Tf)$_2$] (Tf = $N(SO_2CF_3)_2$) was described elsewhere.[18]

To synthesize $Sn_3I_8\cdot 2$(18-crown-6), 100 mg (1.60 mmol) of SnI_4, 119 mg (3.19 mmol) of SnI_2, and 84 mg (3.18 mmol) of 18-crown-6 were reacted in 2 mL of [NMe(n-Bu)$_3$][N(Tf)$_2$] at 393 K for 24 h. Black, plate-shaped crystals were obtained after cooling to room temperature with a ratio of 5 K/h. The crystals were separated from the ionic liquid by filtration through a glass filter and by washing three times with 4 mL of dried tetrahydrofuran. Finally, $Sn_3I_8\cdot 2$(18-crown-6) was dried in vacuum and obtained with a yield of about 70 %.

Single crystal X-ray diffraction analysis was conducted with an IPDS I diffractometer (STOE, Darmstadt) using Mo K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator). A suited crystal was fixed onto a glass filament and begird in perfluorated oil (Kel-F). Data collection was performed at 200 K. All non-hydrogen atoms were refined with anisotropic parameters of displacement. The position of hydrogen could not be fixed via Fourier refinement and was therefore modeled based on idealized C−H bonds. Additional information concerning data collection, structure solution, and refinement is listed in Tables 1 and 2. A powder diffraction pattern was obtained with a STADI-P diffractometer (Stoe, Darmstadt) using germanium monochromatized Cu $K_{\alpha1}$ radiation. The sample was filled in a glass capillary and measured at ambient temperature. In view of the comparably strong X-ray absorption of the sample and the distinct plate-shaped morphology, the sample was diluted by admixing of non-crystalline silica. Because of the presence of very brittle and smeary microcrystals, the quality of the powder diffraction pattern is nevertheless limited.

A $Ca^{119}SnO_3$ source was available for ^{119}Sn Mössbauer spectroscopy. The sample was diluted with dried SiO_2 and sealed within a thin-walled Pyrex container at a density of about 10 mg Sn/cm^2. A palladium foil (0.05 mm thickness) was used to reduce Sn−K X-rays concurrently emitted by the source. The measurement was conducted with standard transmission geometry at 78 K. The data were collected with a counting time of 2 days.

Results and Discussion

$Sn_3I_8\cdot 2$(18-crown-6) is prepared by reaction of SnI_2, SnI_4, and 18-crown-6 in the ionic liquid [NMe(n-Bu)$_3$][N(Tf)$_2$]. The synthesis results in large quantities of moisture-sensitive, black and plate-shaped crystals. According to X-ray structure analysis based on single crystals, the title compound crystallizes monoclinically with space group $P2/n$. The unit cell displays $[SnI_5]^-$-anions and $[Sn_2I_3(18\text{-crown-}6)_2]^+$-cations as the constituents of $Sn_3I_8\cdot 2$(18-crown-6) (Figure 1). In addition to single-crystal structure analysis, purity and crystal structure of the title compound are validated by a powder diffraction pattern (Figure 2). While studying the thermal properties, interestingly, sublimation of $Sn_3I_8\cdot 2$(18-crown-6) was observed above 100 °C without decomposition. This is most probably because of a dissociative sublimation process via SnI_2, SnI_4, and (18-crown-6) as intermediate gas-phase species.

The constituting $[SnI_5]^-$-anion only exhibits a slight deviation from a trigonal-bipyramidal symmetry (Figure 3). This view is confirmed by angles I_{eq}−Sn−I_{eq} of 120±2°, and I_{ax}−Sn−I_{eq} of 90±1° (Table 2). The Sn−I bond lengths with 273.0 to 287.3 pm are close to those of SnI_4 (263 pm),[19] but differ significantly from those of SnI_2 (300−325 pm).[20] Taking the widened coordination from 4 (SnI_4) to 5 (SnI_5^-) into account, the bond lengths clearly point to the presence

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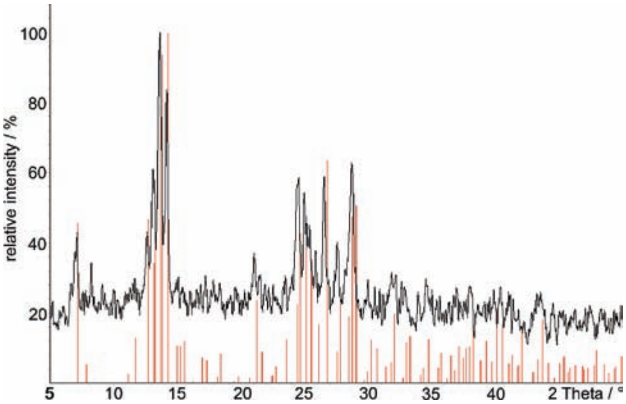

Figure 2. Powder diffraction pattern of $Sn_3I_8 \cdot 2$(18-crown-6) (black) in comparison to a line-pattern calculation based on single crystal structure analysis (red). The sample was diluted with non-crystalline silica.

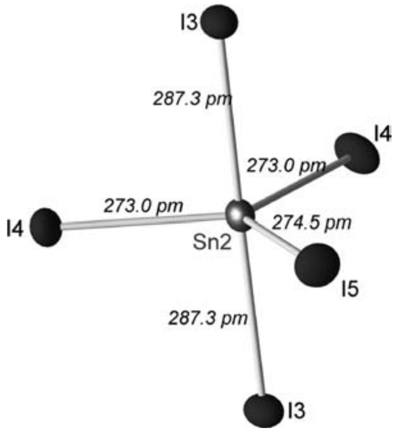

Figure 3. $[SnI_5]^-$-anion in $Sn_3I_8 \cdot 2$(18-crown-6) (thermal ellipsoids drawn with 50 % probability of finding).

of Sn^{4+}. Such a trigonal-bipyramidal coordination, in general, is much less common for iodostannates(IV) than the well-known octahedral coordination.[21,22] Compounds such as $[NH_2C(I){=}NH_2]_3[SnI_5]$ or $[CH_3SC(NH_2)_2]_3[SnI_5]$ actually contain corner-sharing $[SnI_4I_{2/2}]^-$ octahedra.[24,23,24] In fact, iodostannates(IV) are characterized by merged building units. Only $[SnI_6]^{2-}$ has been described as an isolated building unit so far.[25] $[SnI_5]^-$ as an isolated building unit is first identified here.

The cation $[Sn_2I_3(\text{18-crown-6})_2]^+$ is also presented first here. It consists of two symmetry equivalent crown-ether molecules, each of them entrapping a tin atom (Figure 4). Herein, Sn^{2+} is positioned endocyclically inside the crown-ether molecule plane. On the other hand, Sn^{2+} is deflected from the center of the crown ether (Figure 5), resulting in three shortened (261−267 pm) and three lengthened Sn−O (276−293 pm) distances (Table 2). This finding might be due to two reasons. On the basis of an ionic model, the radius of Sn^{2+} (93 pm for 6-fold coordination) is too small with respect to the opening of the crown ether, which is well known to fit exactly to the much larger K$^+$ (138 pm for 6-fold coordination).[26−28] A certain decentering of Sn^{2+} is therefore expected with regard to the optimal Coulomb interaction. In addition to this electrostatic argumentation, deflection of Sn^{2+} may also be triggered by a lone-pair effect that is observed quite often for divalent tin.[29] Crown ether coordination of Sn^{2+} has been already described, for instance, in $[Sn(\text{18-crown-6})Cl][SnCl_3]$.[30] Here, a comparable situation with Sn−O bond lengths ranging from 257−288 pm is observed. In contrast, complexes of Sn^{4+} and 18-crown-6 are characterized by an exocyclic coordination.[31]

In addition to 18-crown-6, each Sn^{2+} is coordinated to a terminal iodine atom, as well as to a joint bridging I$^-$ (Figure 4). This connectivity results in a V-shaped $[Sn_2I_3]$-helix exhibiting angles of 165.3° (I−Sn−I) and 142.1° (Sn−I−Sn). Note that the Sn−I bond lengths differ significantly. Namely, a short distance to terminal iodine (287 pm) and a much longer distance to the bridging one (355 pm) is observed (Table 2). As a consequence, the cation can also be described as an $[(\text{18-crown-6})SnI]^+$. Herein, 18-crown-6 is arranged almost orthogonal to the Sn1−I1 bonding axis. With regard to the valence state of tin, the bond lengths are indifferent when comparing them to the binary compounds SnI_2 (300−325 pm)[20] and SnI_4 (263 pm).[19] Only the mean distance (321 pm) hints to Sn^{2+}. Finally, all C−O and C−C bond lengths of 18-crown-6 match with the expected values.[32]

Although the electrostatic description of $Sn_3I_8 \cdot 2$(18-crown-6) based on $[SnI_5]^-$-anions and $[Sn_2I_3(\text{18-crown-6})_2]^+$-cations is valuable, the formation of an infinite three-dimensional network via long-ranging I−I contacts is obtained. Such long-ranging but still attractive interactions are well known from the so-called polyiodides.[33] In the case of the title compound attractive bonding with distances below the doubled van der Waals radius of iodine (i.e., 420 pm)[34] are indicated between I1 and I3 (409 pm), as well as between I2 and I4 (406 pm). I5 remains as the only non-coordinating iodine atom. Altogether, attractive iodine-driven interaction between $[Sn_2I_3(\text{18-crown-6})_2]^+$ and $[SnI_5]^-$ thus leads to an infinite zig-zag type structure along [001] and [100].

The observed bond distances, as well as electroneutrality, have already pointed to a mixed-valent tin compound; however, a final proof is not possible based on a single-crystal structure analysis. Hence, a presence of excessive electrons in the conduction band can not be excluded. On the other hand, deflection of tin entrapped inside the crown ether, as well as the tilted I2−Sn1−I1 bonding axis (165°),

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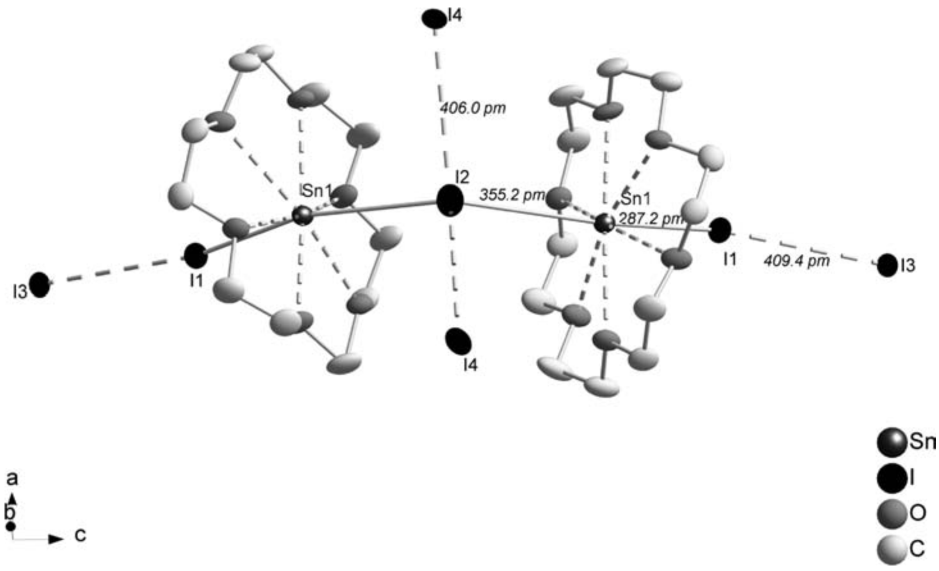

Figure 4. $[Sn_2I_3(18\text{-crown-}6)_2]^+$-cation in $Sn_3I_8 \cdot 2(18\text{-crown-}6)$ (thermal ellipsoids drawn with 50 % probability of finding).

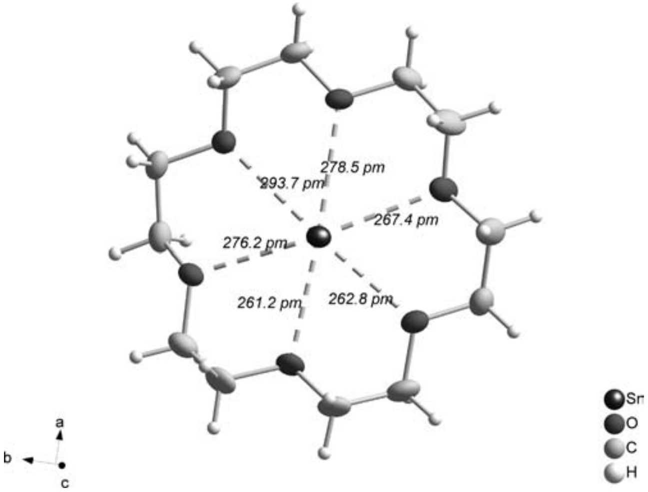

Figure 5. Sn^{2+} coordinated by (18-crown-6) (thermal ellipsoids drawn with 50 % probability of finding).

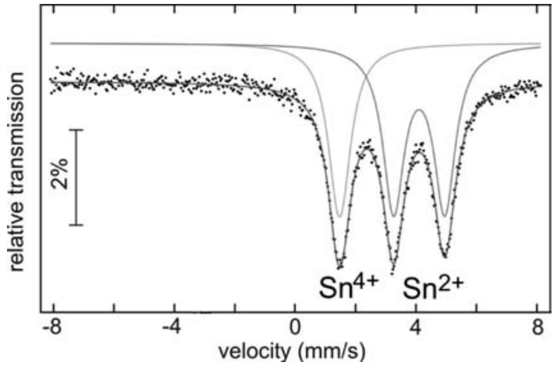

Figure 6. ^{119}Sn-Mössbauer spectrum of $Sn_3I_8 \cdot 2(18\text{-crown-}6)$.

point to a stereochemically active lone pair and thereby to Sn^{2+}. To ensure the assumption of mixed valency ^{119}Sn-Mössbauer spectroscopy was used. A spectrum of $Sn_3I_8 \cdot 2(18\text{-crown-}6)$ was recorded at 78 K and is displayed in Figure 6 together with a transmission integral fit. The spectrum was well reproduced with two signals at isomer shifts of $\delta = 1.474(4)$ and 4.108(3) mm/s with experimental line widths of $\Gamma = 0.83(3)$ and 0.853(8) mm/s, respectively. These two signals occur in a ratio of 35(1)/65(1), in agreement with the crystal structure data. The signal at $\delta = 1.474(4)$ is indicative of tetravalent tin, in agreement with the shift observed for SnI_4 (1.5 mm/s).[35] The second signal can clearly be attributed to divalent tin, similar to SnI_2 which has an isomer shift of 3.9 mm/s. While no quadrupole splitting parameter was needed for the Sn(IV) site (although one would expect very weak quadrupole splitting because of the non-cubic site symmetry), the Sn(II) site was subject to significant quadrupole splitting of 1.688(6) mm/s, a clear evidence for the non-cubic site symmetry and the lone pair stereochemical activity.[35,36]

In summary, with $Sn_3I_8 \cdot 2(18\text{-crown-}6)$ a novel mixed-valent iodostannate is prepared applying ionic liquids as a solvent. The title compound consists of isolated, trigonal-bypyramidal $[SnI_5]^-$-anions and V-shaped $[Sn_2I_3(18\text{-crown-}6)_2]^+$-cations. Both constituents have not been obtained before. The mixed valence state of tin is evidenced in terms of electroneutrality and bond length considerations, as well as by ^{119}Sn−Mössbauer spectroscopy.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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