

Coordination Chemistry

International Edition: DOI: 10.1002/anie.201911126
German Edition: DOI: 10.1002/ange.201911126**[SnI₈{Fe(CO)₄]₄]²⁺: Highly Coordinated Sn^{+II}I₈ Subunit with Fragile Carbonyl Clips**

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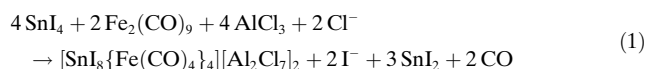
Dedicated to Professor Arndt Simon on the occasion of his 80th birthday

Abstract: [SnI₈{Fe(CO)₄]₄][Al₂Cl₇]₂ contains the [SnI₈{Fe(CO)₄]₄]²⁺ cation with an unprecedented highly coordinated, bicapped SnI₈ prism. Given the eightfold coordination with the most voluminous stable halide, it is all the more surprising that this SnI₈ arrangement is surrounded only by fragile Fe(CO)₄ groups in a clip-like fashion. In spite of a predominantly ionic bonding situation in [SnI₈{Fe(CO)₄]₄]²⁺, the I⋯I distances are considerably shortened (down to 371 pm) and significantly less than the van der Waals distance (420 pm). The title compound is characterized by single-crystal structure analysis, spectroscopic methods (EDXS, FTIR, Raman, UV/Vis, Mössbauer), thermogravimetry, and density functional theory methods.

High coordination numbers (CNs) are preferably realized at high pressure and with small ligands.^[1] In the solid state, moreover, high CNs are preferred in densely packed structures (e.g. perovskites) and supported by high lattice energies. For cationic tin (Sn²⁺, Sn⁴⁺), flexible coordination is possible and most often refers to tetrahedral and octahedral arrangements.^[2] To date, higher CNs are known only for chelating ligands (e.g. crown ethers)^[3] or chelating oxoanions at high pressure (e.g. CN 10 in β-SnB₄O₇ made at 7.5 GPa/1100 °C).^[4] In all these cases, multidentate ligands and/or high pressure are a prerequisite. For monodentate ligands, the CN of Sn^{2+/4+} is typically limited to six. The binary SnI₂ shows (5+2) coordination with five shorter (303–326 pm) and two significantly longer Sn–I distances (373 pm).^[5] Even for fluorine, the smallest halide, only sixfold coordination was reported (e.g. [NH₄]₃[SnF₆]F).^[6] Eightfold coordination with iodine, to the

best of our knowledge, is also unknown for the significantly larger Pb²⁺ ion. With this background, [SnI₈{Fe(CO)₄]₄][Al₂Cl₇]₂ is surprising for several reasons: 1) eightfold halide coordination of Sn²⁺ is observed for the first time; 2) despite its size and repulsive I[−]⋯I[−] interaction, eightfold coordination occurs with the most voluminous stable halide; 3) the SnI₈ building unit is surrounded only by fragile Fe(CO)₄ groups in a clip-like fashion.

[SnI₈{Fe(CO)₄]₄][Al₂Cl₇]₂ was prepared by heating SnI₄ and Fe₂(CO)₉ in the ionic liquid [BMIm]Cl/AlCl₃ (ratio 1:3; [BMIm]: 1-butyl-3-methylimidazolium) to 130 °C in argon-filled, sealed glass ampoules. This temperature was required to dissolve all starting materials. When the reaction mixture was slowly cooled to room temperature (1 K h^{−1}), numerous large black crystals (up to 0.5 mm³) with a slight violet shimmer were obtained starting at about 50 °C (Figure 1; Supporting Information: Figures S1–S5). The reaction can be rationalized by reduction of Sn^{+IV} to Sn^{+II} and oxidation of Fe^{±0} to Fe^{+II} [Eq. (1)]:



An excess of Fe₂(CO)₉ (i.e. SnI₄/Fe₂(CO)₉ = 1:1) supports the crystal quality and leads to higher yields (≈ 50 %) of the title compound. Surprisingly, [SnI₈{Fe(CO)₄]₄][Al₂Cl₇]₂ also is the first compound in the Sn–Fe–I system with iodine interlinking iron and tin. This type of halide-based linkage

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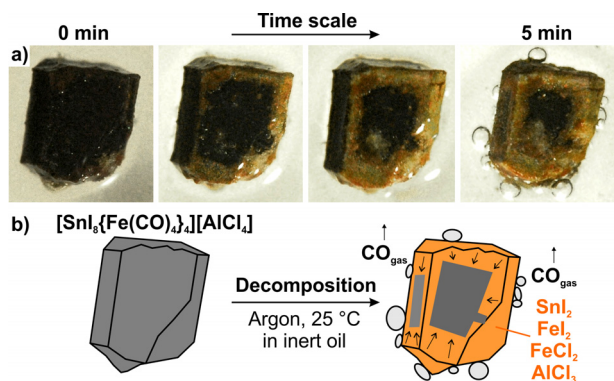


Figure 1. Decomposition of [SnI₈{Fe(CO)₄]₄][Al₂Cl₇]₂ single crystals after separation from the mother liquor (in perfluorinated polyalkyl-ether under argon at 25 °C): a) Photos of a crystal taken over a period of 5 minutes (light microscopy); b) scheme of the decomposition with reaction products.

was previously reported only for chlorine-bridged compounds (e.g. $[\text{Cp}(\text{CO})_2\text{FeClSnCl}_4]$).^[7]

X-ray structure analysis based on single crystals revealed the title compound to crystallize in the monoclinic space group $C2/c$ (Table S1, Figures S2 and S3) and to contain $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cations and $[\text{Al}_2\text{Cl}_7]^-$ anions.^[8] Beside crystal structure analysis, the chemical composition was validated by energy-dispersive X-ray spectroscopy (EDXS) with a Sn/I/Fe ratio of 1.3:8:4.3 (scaled on iodine as the heaviest element) which fits well with the expectation (1:8:4).

$[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4][\text{Al}_2\text{Cl}_7]_2$ turned out to be highly reactive and decomposes immediately in the presence of air and moisture. Whereas single crystals are stable under inert conditions in the ionic liquid, removal from the mother liquor even under argon causes fast decomposition (≤ 5 min) at room temperature (Figure 1), which was stopped only at about -50°C . The decomposition of single crystals at room temperature can be monitored by light microscopy in perfluorinated polyalkylether (Figure 1a). Like a glass of champagne the crystals start forming gas bubbles, which roll off after having reached a certain size. In addition to the evolution of CO, the crystals decolorize within 5 minutes from the surface to the interior (Figure 1). This decolorization from deep black to blotchy orange and white can be ascribed to the following reaction [Eq. (2)]:



The formation of AlCl_3 and SnI_2 is indicated by characteristic colorless needles (AlCl_3) and orange crystals (SnI_2). The lack of any $\text{C}=\text{O}$ vibrations in the FTIR spectra points to the absence of metal carbonyls (e.g., $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $[\text{cis-Fe}(\text{CO})_4\text{I}_2]$) as decomposition products (Figure S1). In contrast to room-temperature decomposition, the heating of the title compound leads to a three-step decomposition between room temperature and 500°C with evaporation of CO, AlCl_3 , I_2 , and SnCl_2 , leaving iron metal as a solid residue (Figure S6). The synthesis temperature of $40\text{--}50^\circ\text{C}$ (in the ionic liquid) and the rapid decomposition under inert conditions at 25°C (and below) illustrate the metastability and fragile nature of the title compound.

The unusual $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation is centered by Sn^{+II} , which in turn is eightfold coordinated by iodide (Figure 2a). The resulting SnI_8 polyhedron can be described as a bicapped triangular prism (Figure 2b,d). The Sn–I distances of 317.3(2)–330.6(3) pm in the prism (Figure 2c) are comparable to those of SnI_2 ^[5] but significantly longer than in SnI_4 (Table 1),^[6] which points to Sn^{+II} and ionic bonding. The Sn–I distances of the two capping iodine atoms of the central SnI_8 subunit (332.0(1), 341.2(3) pm) are slightly longer than the Sn–I distances within the prism (Figure 2c). Even these longer Sn–I distances are nevertheless significantly shorter than the extended distances in SnI_2 (373.4 pm)^[5] and the sum of the Sn–I van der Waals radii (411 pm).^[9] Taking the large volume and the repulsion of the negatively charged I^- neighbors into account, such short Sn–I distances in combination with eightfold coordination in the $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation are unprecedented.

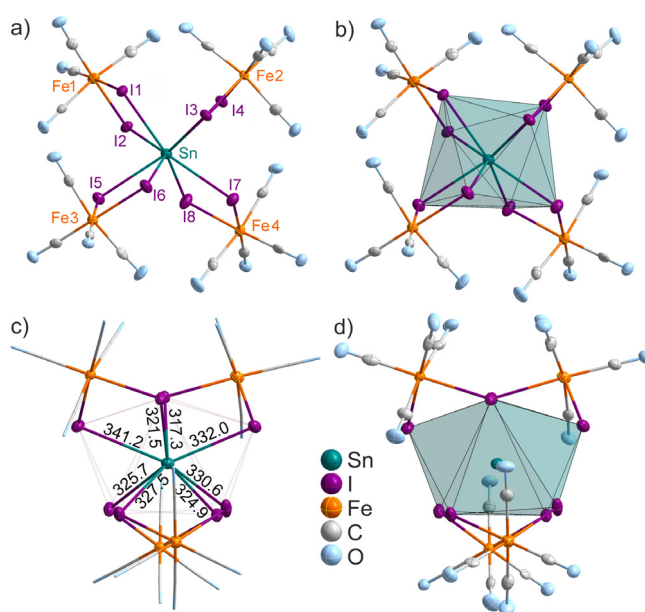


Figure 2. $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation: a) Overview with crystallographic numbering of the atoms; b) side view of the bicapped triangular SnI_8 prism; c) Sn–I distances (in pm); d) top view of the bicapped triangular SnI_8 prism.

Table 1: Selected distances (d) in the $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation according to single-crystal structure analysis and selected references (Py: pyridine; L: $(\mu\text{-TePh})\text{Fe}(\text{CO})_2\text{Cp}$).

Compound	$d(\text{Sn}-\text{I})$ [pm]	$d(\text{Fe}-\text{I})$ [pm]
$[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$	317.3(2)–341.2(3)	262.6(2)–264.9(2)
SnI_2 ^[5]	302.7–325.7	/
	373.4	
SnI_4 ^[10]	269.7	/
FeI_2 (solid) ^[11]	/	288.5
Fe_2I_4 (dimer, gas phase) ^[12a]	/	248.0, 268.3
$[\text{Fe}(\text{CO})_3(\text{Py})\text{I}_2]$ ^[12b]	/	265.5, 266.7
$[\text{Fe}(\text{CO})_3(\text{L})\text{I}_2]$ ^[12c]	/	265.3

The I...I distances in the central SnI_8 subunit cover a wide range and can be assigned to two groups. Pairs of iodine atoms are bridged by $\text{Fe}(\text{CO})_4$ groups in a clip-like fashion and exhibit distances of 376.3–384.4 pm (Figure 3a). The respective Fe–I distances (262.6(2)–264.9(2) pm) are shorter than in solid FeI_2 (288.5 pm)^[11] and compare to those of bridging Fe–I

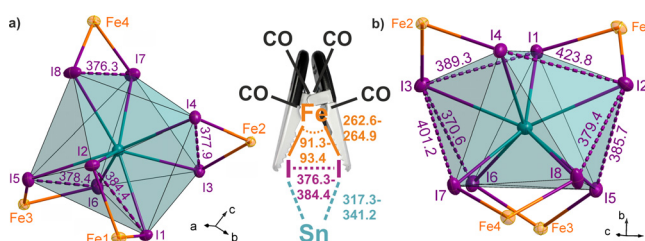


Figure 3. I...I distances (in pm) in the $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation: a) $\text{Fe}(\text{CO})_4$ -clipped pairs of iodide with I–Fe–I angles (in $^\circ$) including schematic illustration, b) non- $\text{Fe}(\text{CO})_4$ -clipped pairs of iodide (for longer I...I distances see: Figure S4).

in the Fe_2I_4 dimer and other carbonyldiiodoiron compounds (Table 1).^[12] A second group of I...I distances relates to non- $\text{Fe}(\text{CO})_4$ -clipped pairs of iodine with shorter (370.6–423.8 pm, Figure 3b) and longer distances (412.6–453.7 pm, Figure S4). Several I...I distances are significantly less than the twofold van der Waals distance of iodine (420 pm).^[13] Such close contacts typically indicate attractive bonding as they are known from iodine-iodide interactions ($\text{I}^{\pm 0}\cdots\text{I}^{-1}$) in polyiodides.^[13] In $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$, however, the close contacts occur between negatively charged iodide atoms ($\text{I}^{-1}\cdots\text{I}^{-1}$). This finding can be attributed predominantly to the $\text{Fe}(\text{CO})_4$ clips since increasing the I...I distance would cause a widening of the I-Fe-I angle, which, however, is more or less constrained to 90° ($91.3(1)$ – $93.4(1)^\circ$).

The $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation could also be formally described as a Sn^{2+} -centered coordination complex with four uncharged $[\text{cis-Fe}(\text{CO})_4\text{I}_2]$ ligands. However, it should be noted that no equilibrium of Sn^{2+} and $[\text{cis-Fe}(\text{CO})_4\text{I}_2]$ was observed—neither for the synthesis nor for the decomposition of the title compound. $[\text{cis-Fe}(\text{CO})_4\text{I}_2]$ as a compound has been barely studied generally and previously characterized predominately by vibrational spectroscopy,^[14] whereas single-crystal structure analysis is still missing. With the viewpoint of a central Sn^{2+} coordinated by fragile $[\text{cis-Fe}(\text{CO})_4\text{I}_2]$ ligands, the existence of a $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation with close iodide contacts and eightfold coordination is still surprising.

The valence states of Sn^{+II} and Fe^{+II} , as already suggested by the chemical composition and distances, were further validated by Mössbauer spectroscopy and Fourier transform infrared spectroscopy (FTIR). ^{119}Sn Mössbauer spectra clearly point to the presence of Sn^{+II} (Table S2 and Figure S7). Unfortunately, ^{57}Fe Mössbauer spectra could not be recorded due to the strong absorption of iodine (see the Supporting Information). With regards to iron, however, FTIR spectra are indicative and show two strong ($2156, 2100\text{ cm}^{-1}$) and two weak ($2115, 2135\text{ cm}^{-1}$) CO vibrations (Figure 4a; Table S3 and Figure S8), which are well in agreement with references such as $[\text{cis-Fe}^{+II}(\text{CO})_4\text{I}_2]$ ($2129, 2084, 2060\text{ cm}^{-1}$).^[14] In contrast, the CO vibrations of zero-valent iron carbonyls like $\text{Fe}(\text{CO})_5$ ($2000, 2025\text{ cm}^{-1}$)^[15] and $\text{Fe}_2(\text{CO})_9$ ($2084, 2034\text{ cm}^{-1}$)^[16] occur at lower wavenumbers. This observation can be ascribed to stronger σ -bonding and weaker π -back-bonding, which confirms the lower electron density and the

positive valence state of iron in $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$. These findings are confirmed by Raman spectroscopy (Figure 4b; Figure S9). With the help of theoretical calculations, Raman bands close to $590, 390, 200,$ and 185 cm^{-1} can be attributed to $\nu(\text{Fe-C})$ and $\delta(\text{Fe-C-O})$ as well as to $\nu_{\text{sym}}(\text{FeI}_2)$ and $\nu_{\text{antisym}}(\text{FeI}_2)$. Calculated Raman spectra of the $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation are also in good agreement with the experimental data (Table S4 and Figure S10).

The structure and bonding of the $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation were finally verified by quantum chemical calculations based on density functional theory (DFT). Accordingly, a square antiprism of SnI_8 with D_4 symmetry turned out to be a local minimum on the potential energy surface (Table S5 and Figure S11). Distortion of the D_4 -symmetric structure, however, resulted in D_{2d} symmetry being 32.5 kJ mol^{-1} more stable than D_4 symmetry. Due to two imaginary vibrational frequencies, however, this D_{2d} structure represents only a saddle point on the potential energy surface, which relaxes to a subgroup with S_4 symmetry (torsion angle I1-Sn1-I8-I2: 15.1°) and a “real” local energy minimum being 1.9 kJ mol^{-1} even more stable (HOMO–LUMO gap: 1.66 eV). Although the potential energy surface is rather flat with regards to the torsion angle, DFT methods indicate that a bicapped trigonal SnI_8 prism is more stable (-34.5 kJ mol^{-1}) than square antiprismatic coordination, which excellently reflects the experimental observation (Table 2, Figure 5; Figure S11). In comparison to a calculated $[\text{cis-Fe}(\text{CO})_4\text{I}_2]$ molecule, the

Table 2: Selected distances (d) and angles (\sphericalangle) in the $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation according to DFT calculations and experimental data (calculated $[\text{cis-Fe}(\text{CO})_4\text{I}_2]$ molecule as a reference).

Species	$d(\text{Sn-I})$ [pm]	$d(\text{Fe-I})$ [pm]	$d(\text{I}\cdots\text{I})$ [pm]	$\sphericalangle(\text{I-Fe-I})$ [$^\circ$]
Calculated (DFT)				
$[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$	333.9	267.9	367.6, 383.9	91.3
$[\text{cis-Fe}(\text{CO})_4\text{I}_2]$	/	267.4	397.1	95.9
Experimental data (single-crystal structure analysis)				
$[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$	317.3(2)– 341.2(3)	262.6(2)– 264.9(2)	370.6(2)– 384.4(2)	91.3(1)– 93.4(1)

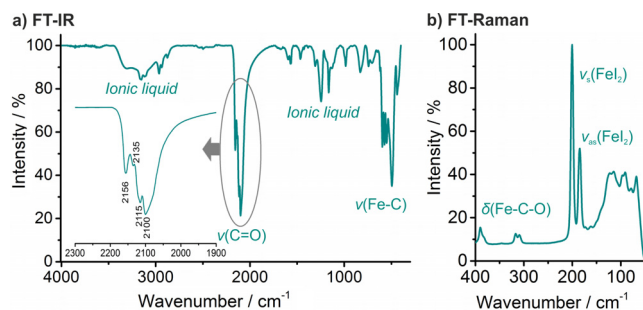


Figure 4. Vibrational spectroscopy of $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4][\text{Al}_2\text{Cl}_7]_2$: a) FTIR spectrum (detailed view of CO vibrations as inset, crystals of the title compound embedded in ionic liquid for stabilization (Figure S8); b) FT-Raman spectrum (Figure S9).

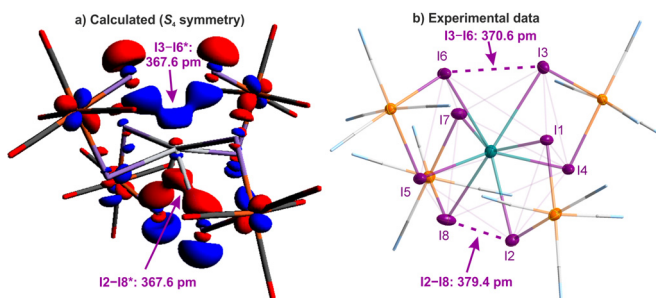


Figure 5. Bonding in $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ with regard to the shortest I...I contacts: a) Calculated bonding MO (DFT) indicating a slight electron transfer from nonbonding iodide electron pairs into the formally vacant valence p atomic orbital of Sn^{2+} (isosurface values at ± 0.04 ; *calculated I2...I8/I3...I6 are symmetry equivalent due to S_4 symmetry); b) Experimental data (single-crystal structure analysis).

larger I...I distance and I-Fe-I angle in $[cis\text{-Fe}(\text{CO})_4\text{I}_2]$ are noticeable and point to the strong influence of tin in $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$.

With regard to the I...I distances, DFT calculations confirm the variability of distances and the presence of short I...I contacts in the S_4 -symmetric $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation for the $\text{Fe}(\text{CO})_4$ -clipped and non- $\text{Fe}(\text{CO})_4$ -clipped pairs of iodine (Table 2). To verify whether the shortest I...I distances result from attractive interactions, Bader AIM analysis was performed (AIM: atoms in molecules; see the Supporting Information). Here, bond-critical points (electron density ρ_{BCP} : 0.012) were observed only for the I3...I6/I2...I8 couple (367.6 pm) (Figure 5 a, Figure S12). The electron density at this bond-critical point, however, is four to five times lower than for the polyiodide I_5^- (ρ_{BCP} : 0.052, 0.038), which was calculated as a reference system (Figure S13). Moreover, this weak interaction does not result from direct I...I bonding but from slight electron transfer of nonbonding electron pairs on iodide to the formally vacant valence p atomic orbital of Sn^{2+} (Figure 5 a; Figure S14). All additional I...I contacts in the central SnI_8 subunit did not result in bond-critical points. In comparison to the calculated distances, finally, the respective I...I distances in the experimentally observed non- S_4 -symmetric $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation (I3...I6: 370.6, I2...I8: 379.4 pm) are in part significantly longer (Table 2, Figure 5 b). Taken together, the influence of attractive I...I interactions can be considered to be negligible.

Based on the results of DFT calculations, the bonding situation in $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ is predominantly ionic in nature. This ionic bonding was further confirmed by Ahlrichs–Heinzmann population analysis (Table S6),^[17] which results in the “ionic” fragments Sn, I, and $\text{Fe}(\text{CO})_4$ with partial charges of +0.27, -0.07, and +0.57, respectively. Thus, the bonding situation in $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ can be best described by a predominately ionic interaction of tin and iodine and a predominately covalent interaction of iodine and iron, where, of course, contributions of both bonding types are included in all cases. Further stabilization of $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4][\text{Al}_2\text{Cl}_7]_2$ results from lattice energy and the long-range cation–anion interaction.

In summary, $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4][\text{Al}_2\text{Cl}_7]_2$ is a novel carbonyl compound that was synthesized in an ionic liquid. The title compound is highly sensitive and decomposes rapidly (≤ 5 min) after removal from the mother liquor under argon even at room temperature. The fact that its temperature of decomposition ($\leq 25^\circ\text{C}$) is below the temperature of synthesis ($40\text{--}50^\circ\text{C}$) points to the metastable nature of $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4][\text{Al}_2\text{Cl}_7]_2$. Most remarkable is the $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation with a central bicapped SnI_8 prism and an unusually high eightfold coordination of Sn^{+II} . Comparably short I...I contacts (down to 371 pm) are observed despite the negatively charged iodide and negligible attractive I...I interactions. The existence of this predominately ionic, Sn^{2+} -centered $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4]^{2+}$ cation with fragile $\text{Fe}(\text{CO})_4$ clips, eightfold coordination of tin, and short iodide–iodide contacts is unprecedented. The synthesis in weakly coordinating ionic liquids near room temperature seems to be essential to obtain such a fragile compound at the border between formation and decomposition.

Experimental Section

Chemicals. All sample handling was strictly conducted under argon, applying standard Schlenk or glovebox techniques. Reactions were performed in argon-filled and sealed glass ampoules, which were dried under reduced pressure (1×10^{-3} mbar) at 300°C prior to use. $\text{Fe}_2(\text{CO})_9$ (99.99%, ABCR) and AlCl_3 (99.99%, ABCR) were used as supplied. SnI_4 was synthesized by reacting Sn and I_2 in toluene. $[\text{BMIm}]\text{Cl}$ (99%, IoLiTec) was dried under vacuum at 130°C for 30 hours prior to use.

$[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4][\text{Al}_2\text{Cl}_7]_2$. SnI_4 (80 mg, 0.13 mmol) and $\text{Fe}_2(\text{CO})_9$ (45.5 mg, 0.13 mmol) were added to a 1:3 mixture of $[\text{BMIm}]\text{Cl}$ (500 mg, 2.86 mmol) and AlCl_3 (1145 mg, 8.59 mmol) as the ionic liquid. This mixture was heated in sealed glass ampoules at 130°C for 4 days to guarantee the dissolution of all AlCl_3 and all starting materials. When the reaction mixture was cooled to room temperature at a rate of 1 K h^{-1} , the formation of black crystals with a weak violet shimmer was observed at a temperature of $\leq 50^\circ\text{C}$ along with tiny orange needles of SnI_2 . The crystals were separated from the ionic liquid by filtration through a glass frit and washed with the pure ionic liquid to remove unreacted starting materials and SnI_2 . Whereas the title compound was stable in the ionic liquid, its removal from the mother liquor even under inert conditions (argon) and even at room temperature results in rapid decomposition (≤ 5 min). The decomposition with release of CO was decelerated at lower temperature and stopped at about -50°C .

Further details regarding synthesis, crystal structure analysis, spectroscopic characterization, and quantum chemical calculations can be obtained from the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbonyl ligands · ionic liquids · SnI_8 · tin iodide

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