The X-Ray Structure of $[\{Sn(\eta-C_5Me_5)\}\}$ $\{Sn(\eta-C_5Me_5)(O_3SCF_3)_2\}]$

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This paper reports the interesting structure of an ionic aggregate which exists as proposed only in the solid state. Once in solution it dissociates into $Sn(\eta-C_5Me_5)^+$ cations and CF_3S O_3^- anions. Solid state NMR spectroscopic results give support to the proposed observation.

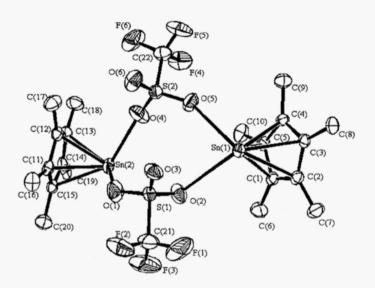


Figure 1: The molecular structure of [$\{Sn(\eta-C_5Me_5)\}\{Sn(\eta-C_5Me_5)(O_3SCF_3)_2\}$] 1 and atom numbering scheme with selected bond lengths (Å) and angles (°): Sn(1)-M(1) 2.181(4), Sn(1)-C(1) 2.536(4), Sn(1)-C(2) 2.510(4), Sn(1)-C(3) 2.474(3), Sn(1)-C(4) 2.457(4), Sn(1)-C(5) 2.495(4), Sn(1)-O(2) 3.074(3), Sn(1)-O(5) 2.781(3), Sn(2)-M(2) 2.199(4), Sn(2)-C(11) 2.445(4), Sn(2)-C(12) 2.424(4), Sn(2)-C(13) 2.514(4), Sn(2)-C(14) 2.609(4), Sn(2)-C(15) 2.548(4), Sn(2)-O(4) 2.585(3), Sn(2)-O(1) 2.574(3); M(1) denotes the centroid of the ring C(1) to C(5), M(2) denotes the centroid of the ring C(11) to C(15).

COMMENT

The X-ray crystallographic determination revealed that 1 is formed by an anionic and cationic aggregation of $\{Sn(\eta-Cp^*)\}^+$ and $[Sn(\eta-Cp^s)(OSO_2CF_3)_2]^-$ fragments. It is because the Sn atoms interact unequally with the O atoms of both triflate groups. There are two distinct Sn-O interactions, Sn(1)-O(2), Sn(1)-O(5) av. 2.927 Å and Sn(2)-O(1), Sn(2)-O(4); av. 2.579 Å, respectively. Each triflate group interacts more strongly with Sn(2) than Sn(1), which is weakly coordinated by a second oxygen atom of each triflate group leading to interaction. With respect to the Sn-cyclopentadienyl interactions, the cationic Sn(1)-centroid distance, 2.181(4) Å, is considerably shorter than the Sn-centroid distances observed for Sn(2)-centroid 2.217(6) Å. The solid state ¹¹⁹Sn NMR spectrum of 1 confirmed the X-ray results since two resonances, were observed, δ_{iso} -2097, -2283, which were assigned to the cationic Sn(1) and to the anionic Sn(2), respectively. In solution only one resonance at δ -2170 was observed in the ¹¹⁹Sn NMR spectra, suggesting that compound 1 behaves differently in solution and in the solid state.

EXPERIMENTAL

Preparation: Compound 1 was prepared according to the procedure published by us previously /1/ and based on other works /2/. Yield 68%. (0.95g, 2.36 mmol). Mp 136-138 °C. 1 H NMR (C₆D₆, 400.13 MHz), δ 1.8; 13 C{ 1 H} NMR (C₆D₆, 100.61 MHz), δ 121 (q, 1 J_{C-F} 320 Hz), 118.9 (1 J_{C-Sn} 41 Hz), 10 (2 J_{C-Sn} 10 Hz); 119 Sn{ 1 H} NMR (C₆D₆, 149.21 MHz), δ -2166; 119 Sn{ 1 H} MAS (149.21 MHz), δ -2097, -2283. EI-MS: M 1 *m/z* 404, M $^{+}$ -SO₃CF₃ *m/z* 254, M $^{+}$ -SnSO₃CF₃ *m/z*, 135. Elemental analysis for C₂₂H₃₀F₆O₆S₂Sn₂: C 32.70(32.78), H 3.69(3.72).

Crystallography: The data were collected using a Siemens 3 diffractometer equipped with SMART CCD area detector; graphite-monochromated Mo-K α . The structure was solved by direct methods with SHELXTL version 5.0 /3/ and the refinements were carried out using SHELXTL96 software /4/, minimizing on the weighted R factor wR2. All non-H atoms were anisotropic; methyl hydrogens were included in riding mode with idealised geometry, but with the torsion angle defining the H atom positions refined and with Uiso(H) equal to 1.5Ueq(C).

Table 1

Crystal data and structure refinement for compound 1.

Empirical formula	$C_{22}H_{30}F_6O_6S_2Sn_2$	Formula weight	806.0
Crystal system	monoclinic	Crystal size	0.30 x 0.30 x 0.20 mm
Space group	P2 ₁ /c (Nº 14)	A	11.382 (4) Å
ь	11.676 (3) Å	С	22.352 (8) Å
β	97.46(5)°	Volume	2945 (2) Å ³
Z	4	Diffractometer	Siemens 3
Temperature	173(2) K	Wavelength	0.71073
Density (calc.)	1.82 Mg.m ⁻³	Absorp. coefficient	1.91 mm ⁻¹
F(000)	1584	θ range	2 to 25 deg.
Reflections collected	5446	Independent reflections	5179 [R(int) = 0.0238]
Reflections with I >	4264	Structure solution	Direct methods
2σ (Ι)			
Refinement method	Full-matrix least- squares on all F ²	Data/restraints/parameters	5179 / 0 / 353
Goodness-of-fit on F^2	1.058	Final R indices $[I > 2\sigma(I)]$	R1 = 0.034, $wR2 = 0.076$
R indices (all data)	R1 = 0.047, wR2 = 0.081	Largest diff. Peak and hole	0.50 and -0.45 e.Å-
Abs. Correction	Tmax = 1.00, Tmin = 0.83	Maximum shift/e.s.d.	0.007
CCDC reference	120386		

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