

Table 1
Geometries of the Sn complexes ^{a,b,c)}

Compound	Sn-C	C-H	Sn-H	Sn-Cl	∠ CSnC	∠ HCSn	∠ HSnC	∠ ClSnC	∠ HSnH	∠ ClSnCl
SnH ₄	-	-	1.680*	-	-	-	-	-	109.47	-
SnMeH ₃	2.150	1.080*	1.680*	-	-	111.7*	108.0*	-	110.9*	-
SnMe ₂ H ₂	2.153	1.080	1.680	-	104.8	111.7	108.0	-	119.1	-
SnMe ₃ H	2.147	1.086	1.705	-	107.5	111.6	111.5	-	-	-
SnMe ₄	2.134	1.086*	-	-	109.47	111.6*	-	-	-	-
SnMe ₃ Cl	2.108	1.125	-	2.354	114.9	113.4	-	103.2	-	-
SnMe ₂ Cl ₂	2.109	1.100*	-	2.327	114.9	109.47*	-	99.6*	-	104.7*
SnMeCl ₃	2.104	1.100	-	2.306	-	107.5	-	113.9	-	104.7
SnCl ₄	-	-	-	2.281	-	-	-	-	-	109.47

^{a)} The lengths are in Å and the angles in deg. ^{b)} Ref. [12].

^{c)} The values with an asterisk are estimated from those of similar compounds.

Table 2
Diamagnetic and paramagnetic contributions, σ^{dia} and σ^{para} , to the Sn nuclear magnetic shielding constant σ and their analyses into core and valence MO contributions and into s, p and d AO contributions of Sn and the ligand AO (in ppm)

Compound	σ^{dia}							total	shift
	MO contributing		AO contribution						
	core	valence	Sn(s)	Sn(p)	Sn(d)	ligands			
SnH ₄	5041	55	2371	1805	892	28	5096	124	
SnMeH ₃	5049	77	2370	1804	892	60	5126	94	
SnMe ₂ H ₂	5058	99	2370	1803	892	92	5157	63	
SnMe ₃ H	5066	122	2369	1802	893	124	5188	32	
SnMe ₄	5075	145	2369	1802	893	156	5220	0	
SnMe ₃ Cl	5106	145	2369	1801	893	188	5251	-31	
SnMe ₂ Cl ₂	5141	142	2369	1802	893	219	5283	-63	
SnMeCl ₃	5171	146	2369	1802	894	252	5317	-97	
SnCl ₄	5204	146	2368	1802	894	286	5350	-130	

Compound	σ^{para}					σ^{total}		Exptl. shift		
	MO contribution		AO contribution ^{a)}			total	shift			
	core	valence	Sn(p)	Sn(d)	ligands					
SnH ₄	-85	-1328	-1242	-170	-1	-1413	-599	3683	-475	-
SnMeH ₃	-104	-1464	-1357	-199	-12	-1568	-444	3558	-350	-346
SnMe ₂ H ₂	-123	-1588	-1463	-225	-23	-1711	-301	3446	-238	-225
SnMe ₃ H	-145	-1714	-1571	-252	-36	-1859	-153	3329	-121	-105
SnMe ₄	-179	-1833	-1675	-288	-49	-2012	0	3208	0	0
SnMe ₃ Cl	-184	-1870	-1766	-248	-40	-2054	42	3197	11	154-166
SnMe ₂ Cl ₂	-205	-1850	-1815	-206	-34	-2055	43	3228	-20	137
SnMeCl ₃	-214	-1805	-1818	-173	-28	-2019	7	3298	-90	6
SnCl ₄	-228	-1712	-1763	-158	-19	-1940	-72	3410	-202	-150

^{a)} For the paramagnetic term, the Sn (s) AO contribution vanishes identically because the s electron does not have an angular momentum.

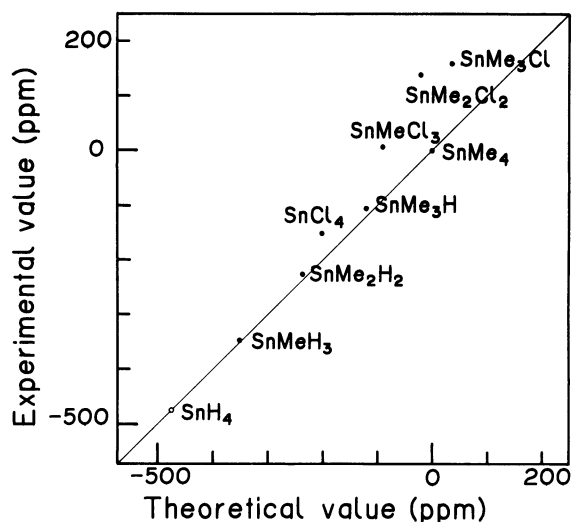


Fig. 1. The correlation between the experimental and theoretical values of the ^{119}Sn chemical shifts of the tin complexes. For SnH_4 , the experimental value is not available so that the open circle shows only the theoretical value.

the diamagnetic and paramagnetic contributions are comparable. It is known that only the structural factor is important for the diamagnetic term [4,5,16]. So, for the chemical shifts of the $\text{SnMe}_{4-x}\text{Cl}_x$ compounds, both the structural and electronic factors are important, though only the latter is important for the $\text{SnMe}_{4-x}\text{H}_x$ compounds.

We next examine the AO and MO analyses of the paramagnetic term. For the $\text{SnMe}_{4-x}\text{H}_x$ compounds, the valence p AO contribution of the Sn atom is dominant (p mechanism), and the d electron contribution is small. This is understood since the 4d-5s and 5s-5p level splittings in the Sn ion are 9.5 and 22.6 eV, respectively [17]. The p orbitals of the Sn atom would therefore mix more easily with the metal-ligand bonds than the d orbitals. For the $\text{SnMe}_{4-x}\text{Cl}_x$ series, the valence MO contribution is the main one likewise, but both the p and d electron contributions are important. In other words, the p electron contribution is suppressed in comparison with the $\text{SnMe}_{4-x}\text{H}_x$ series. This relative increase of the d mechanism is attributed to the change in the hybrid bonding nature of the Sn atom from sp^3 to sd^3 with an increasing number of Cl ligands.

For the $\text{SnMe}_{4-x}\text{H}_x$ series, the chemical shift changes linearly with the change in x , but in the

$\text{SnMe}_{4-x}\text{Cl}_x$ series, it changes in a U-shape. The present theoretical results reproduce this general behavior. The U-shape dependence on x in the $\text{SnMe}_{4-x}\text{Cl}_x$ series is attributed to the dual importance of the p and d mechanisms and also to the importance of the diamagnetic structural factor. More details of the present study will be published in a separate paper.

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