

Experimental Section

All manipulations unless stated otherwise, were carried out under a dry dinitrogen atmosphere using standard Schlenk technique.

Synthesis of compounds

$\text{Cp}_2\text{Ti}(\text{SH})_2$ (**1**) (0.202g, 0.827 mmol) was treated with Me_2SnCl_2 (0.182, 0.827mmol) and Et_3N (0.202g, 0.831mmol) in 20 ml CHCl_3 . Even after 4h of stirring there was no change in the concentration of Me_2SnCl_2 in the reaction mixture.

Compound **2** was obtained by the reaction of **1** (0.244g, 1 mmol) with butyltin chloride dihydroxide (0.245, 1 mmol) in 25 ml benzene. The reaction mixture was refluxed at 80 °C for 14 hours. The precipitate (0.110 g) was filtered off and was found to be insoluble in common organic solvents. The filtrate was concentrated to give yellow-orange colored precipitate which on recrystallization gave yellow colored single crystals of **2** (and **2a**) suitable for X-ray crystallography (Yield.17%). M.P. 160°C (dec). Anal. calcd. for $\text{C}_{54}\text{H}_{90}\text{Cl}_2\text{O}_8\text{S}_{12}\text{Sn}_6\text{Ti}_6$: C, 27.93; H, 3.91. Found: C, 27.99; H, 3.88. IR, (KBr, cm^{-1}), 3092, 2958, 2922, 2860 (ν_{CH}); 1016 (δ_{CH}); 620 ($\nu_{\text{Ti-O}}$) (ν_{SH} was not observed¹). ^1H NMR, (DMSO- D_6 , DMSO at 2.57 ppm) 0.94-1.72 (m, Bu); 3.02 (s, SH); 6.54 (s,Cp); 6.62(s,Cp). ^{13}C NMR (DMSO at 39.50 ppm), 13.74, 25.11, 27.34, 32.61 (Bu); 133.24, 133.39 (Cp). ^{119}Sn NMR, (external reference SnMe_4 at 0 ppm), -122.4. Compound **3** was also obtained as yellow-orange crystals from the same mother liquor (Yield. 5%). Anal. Calcd. For $\text{C}_{54}\text{H}_{90}\text{O}_8\text{S}_{10}\text{Cl}_6\text{Ti}_6\text{Sn}_6$ C,27.02; H,3.78, found: C, 26.97; H, 3.79.

Spectral studies.

^1H , ^{13}C and ^{119}Sn NMR spectra were recorded in CDCl_3 on a JEOL AL300 FT NMR spectrometer.

X-ray Crystallography

Single-crystal X-ray data of **2** and **2a** were collected on a Xcalibur Eos (Oxford) diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data for **2** were collected at low temperature (150°C) while those for **2a** were collected at room temperature (20°C). The data integration and reduction were processed with CrysAlis Pro software.

In spite of our best efforts for more than a year good quality single crystals of **3** could not be grown. X-ray diffraction data from the available single crystals were recorded at room temperature (at IIT Kanpur, India) using a Bruker smart CCD diffractometer. The data reduction was carried out using SAINT+ software.²

All the structures were solved by the direct method and then refined on F^2 by the full matrix least-squares technique with the SHELXL-97 software³ using the WinGX (version 1.70.01) program package.⁴ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as riding atoms using SHELX default parameters. Since the data collections for 2a and 3 were done at room temperature. As a consequence, the thermal ellipsoids on the carbon atoms are large moreover there were several disordered atoms on the *n*-Bu groups some of which (in the case of 3) could not be resolved properly. The structure refinement could, however, be done to clarify the connectivities of atoms.

Theoretical Calculations

All theoretical calculations were carried out using GAUSSIAN 03W set of programs.⁵ Initial atomic coordinates were taken from the X-ray crystallographic data. Structure of the cation was then fully optimized at PBE1 level using 6-31+G** (for C,H,O and Ti atoms) For the anions, optimization were carried at the same level using same basis sets for C,H, S and Cl atoms while LANL2DZ was used for the Sn atoms. Further, *n*-Bu groups have been replaced by Me groups in order to reduce calculation time. NBO analyses⁶ were performed using the optimized atomic coordinates at the same level for the cation. LANL2DZ was used as the basis set for all the atoms while performing the calculations for the anions. Some of the NBO calculations have been repeated using B3LYP functional, however, the results obtained were similar to those obtained when PBE1 was used.

Fig. S1:

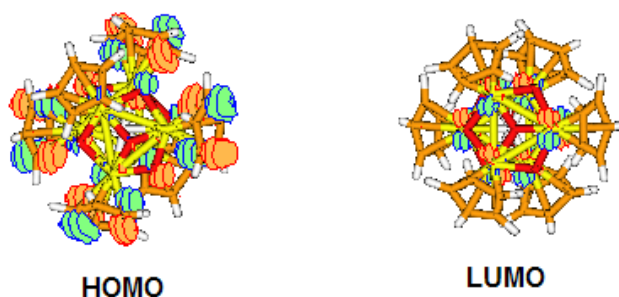


Fig. S2:

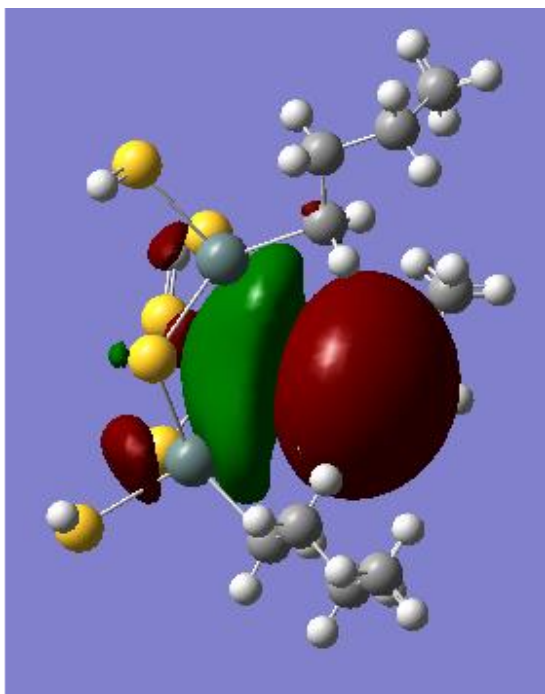


Fig. S3:

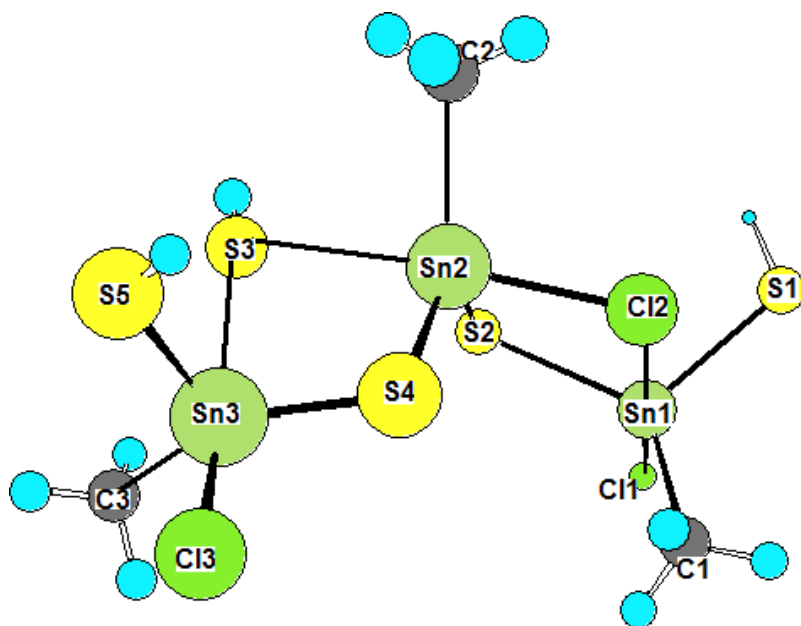


Table S1 Crystal structure and refinement data for the compounds **2**, **2a** and **3**

Compound	2	2a	3
Molecular formula	C ₅₄ H ₉₀ Cl ₂ O ₈ S ₁₂ Sn ₆ Ti ₆	C ₁₀₈ H ₁₈₀ Cl ₄ O ₁₆ S ₂₄ Sn ₁₂ Ti ₁₂	C ₁₀₈ H ₁₈₀ Cl ₁₂ O ₁₆ S ₂₀ Sn ₁₂ Ti ₁₂
Formula weight	2322.42	4644.84	4800.20
Space group	<i>Pbca</i> orthorhombic	<i>P2₁3</i> cubic	<i>P2₁/c</i> monoclinic
A (Å)	19.115(3)	20.2798(8)	21.687(5)
b (Å)	19.488(3)	20.2798(8)	20.079(5)
C (Å)	21.356(2)	20.2798(8)	22.800(5)
V(Å ³)	7955.1(19)	8340.5(6)	9030(4)
Absorption coefficient(μ)	2.841	2.710	2.576
F(000)	4544	4544	4688
Crystal size (mm)	0.20 x 0.18 x 0.10	0.18x 0.08 x 0.06	0.20 x 0.12 x 0.1
2θ range	2.16- 28.54	2.24- 28.45	2.06- 28.55
Index ranges	27 ≤ h ≤ 28 -29 ≤ k ≤ 29 -31 ≤ l ≤ 32	-15 ≤ h ≤ 14 -10 ≤ k ≤ 25 -27 ≤ l ≤ 11	-29 ≤ h ≤ 19 -26 ≤ k ≤ 24 -29 ≤ l ≤ 30
Goodness of fit	1.157	1.118	0.809
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R ₁ =0.0836 wR ₂ =0.1605	R ₁ =0.1063 wR ₂ =0.1647	R ₁ =0.0654 wR ₂ =0.1392

Table S2. Atomic coordinates of the optimized structure of $[\text{Cp}_6\text{Ti}_6\text{O}_8]^{2+}$

Sr. No.	Atomic No.		Atomic Coordinates		
1	6	0	2.789530	2.197704	-2.535531
2	6	0	2.181219	3.286313	-1.858016
3	6	0	2.733525	3.353811	-0.551755
4	6	0	3.684038	2.307441	-0.423927
5	6	0	3.718659	1.594196	-1.649295
6	22	0	1.555364	1.294457	-0.714231
7	8	0	0.658041	1.796436	0.967919
8	22	0	-1.236842	1.704338	0.410508
9	6	0	-3.405137	2.636868	0.692366
10	6	0	-2.771247	3.350617	-0.357654
11	6	0	-1.655029	4.034744	0.187380
12	6	0	-1.597258	3.744724	1.575841
13	6	0	-2.679505	2.880151	1.888582
14	22	0	-0.820241	-0.112067	-1.978296
15	6	0	-2.434040	0.594224	-3.576399
16	6	0	-2.559645	-0.812363	-3.442607
17	6	0	-1.355400	-1.406557	-3.900891
18	6	0	-0.484200	-0.366038	-4.318048
19	6	0	-1.151285	0.871313	-4.117351
20	22	0	-1.545091	-1.294865	0.721568
21	6	0	-2.567445	-3.445190	0.736098
22	6	0	-2.192790	-3.144715	2.071798
23	6	0	-2.950735	-2.021214	2.497078
24	6	0	-3.792165	-1.628186	1.424144
25	6	0	-3.555387	-2.508184	0.336839
26	22	0	1.234269	-1.707725	-0.416343
27	6	0	1.605496	-3.731912	-1.605363
28	6	0	1.632175	-4.044352	-0.220897
29	6	0	2.740631	-3.376298	0.358767
30	6	0	3.401618	-2.650797	-0.666706
31	6	0	2.700296	-2.870755	-1.881362
32	22	0	0.827667	0.120254	1.978668
33	6	0	2.336014	1.135814	3.511991
34	6	0	1.029328	1.284579	4.043738
35	6	0	0.523395	-0.009349	4.332817
36	6	0	1.518197	-0.958593	3.980037
37	6	0	2.638958	-0.250250	3.472674
38	8	0	0.298978	-1.659975	1.314153
39	8	0	-1.124650	0.301889	1.793357
40	8	0	-2.082597	0.169508	-0.483633
41	8	0	-0.654361	-1.794582	-0.964774
42	8	0	-0.290822	1.662240	-1.313757
43	8	0	1.130243	-0.301469	-1.792830
44	8	0	2.086169	-0.167814	0.484625
45	1	0	4.270326	2.081572	0.456682
46	1	0	1.416543	3.937120	-2.259698
47	1	0	3.022432	-3.403736	1.402833
48	1	0	-3.077427	3.362282	-1.395081
49	1	0	1.431122	-2.032924	4.069321
50	1	0	-1.448160	-3.666293	2.657517
51	1	0	0.873123	-4.081202	-2.320421

52	1	0	-3.418843	-1.337552	-3.047999
53	1	0	0.921104	-4.667566	0.304917
54	1	0	-2.161417	-4.236834	0.120794
55	1	0	-4.486261	-0.798517	1.428701
56	1	0	-3.182257	1.325729	-3.302397
57	1	0	-4.277242	2.005068	0.592042
58	1	0	-0.850638	4.109089	2.268347
59	1	0	2.981077	1.938316	3.180157
60	1	0	-4.036173	-2.464395	-0.631069
61	1	0	4.276172	-2.027382	-0.538345
62	1	0	-2.887747	-1.541029	3.464057
63	1	0	2.945680	-2.441675	-2.843351
64	1	0	-0.455043	-0.231106	4.736927
65	1	0	2.464893	4.067864	0.214938
66	1	0	-0.749885	1.854014	-4.325322
67	1	0	-2.902632	2.464596	2.861873
68	1	0	4.336333	0.732706	-1.865704
69	1	0	-1.135648	-2.465488	-3.913340
70	1	0	0.504968	2.219607	4.188349
71	1	0	0.517407	-0.492937	-4.705748
72	1	0	-0.961649	4.658172	-0.361097
73	1	0	3.557499	-0.687112	3.104704
74	1	0	2.572240	1.873339	-3.544333
75	0	0	0.006720	0.005084	0.000778

Table S3. Results of the second order perturbation theory analysis (in NBO) of the anion of **2** revealing Sn-Cl interactions.

E(2) kcal/mol	E(j) - E(i) Donor NBO (i) a.u.	F(i, j) a.u.	Acceptor NBO (j)
64.	LP (1) Cl 34		/239. BD* (1) Sn 41 - S 47
2.64	0.62	0.037	
64.	LP (1) Cl 34		/242. BD* (1) Sn 42 - S 49
3.98	0.62	0.046	
64.	LP (1) Cl 34		/245. BD* (1) Sn 43 - S 51
2.66	0.62	0.037	
65.	LP (2) Cl 34		/228. BD* (1) C 29 -Sn 41
2.86	0.40	0.031	
65.	LP (2) Cl 34		/234. BD* (1) C 37 -Sn 43
2.47	0.44	0.030	
65.	LP (2) Cl 34		/237. BD* (1) Sn 41 - S 44
1.91	0.36	0.024	
65.	LP (2) Cl 34		/239. BD* (1) Sn 41 - S 47
5.05	0.39	0.040	
65.	LP (2) Cl 34		/240. BD* (1) Sn 42 - S 44
1.20	0.37	0.019	
65.	LP (2) Cl 34		/241. BD* (1) Sn 42 - S 46
1.43	0.36	0.021	
65.	LP (2) Cl 34		/244. BD* (1) Sn 43 - S 46
2.52	0.36	0.027	
65.	LP (2) Cl 34		/245. BD* (1) Sn 43 - S 51
4.55	0.39	0.038	
66.	LP (3) Cl 34		/228. BD* (1) C 29 -Sn 41
1.59	0.41	0.023	
66.	LP (3) Cl 34		/232. BD* (1) C 32 -Sn 42
3.43	0.44	0.035	
66.	LP (3) Cl 34		/234. BD* (1) C 37 -Sn 43
1.94	0.45	0.027	
66.	LP (3) Cl 34		/238. BD* (1) Sn 41 - S 45
3.42	0.38	0.033	
66.	LP (3) Cl 34		/239. BD* (1) Sn 41 - S 47
4.16	0.40	0.036	
66.	LP (3) Cl 34		/242. BD* (1) Sn 42 - S 49
2.61	0.40	0.029	
66.	LP (3) Cl 34		/243. BD* (1) Sn 43 - S 45
3.30	0.38	0.032	
66.	LP (3) Cl 34		/245. BD* (1) Sn 43 - S 51
5.50	0.40	0.042	
67.	LP (4) Cl 34		/161. RY* (3) Sn 41
1.04	0.99	0.030	
67.	LP (4) Cl 34		/165. RY* (3) Sn 42
1.65	0.96	0.037	
67.	LP (4) Cl 34		/169. RY* (3) Sn 43
1.03	1.04	0.031	

67. LP (4)Cl 34	/228. BD*(1) C 29 -Sn 41
1.47 0.59 0.026	
67. LP (4)Cl 34	/232. BD*(1) C 32 -Sn 42
4.16 0.62 0.046	
67. LP (4)Cl 34	/234. BD*(1) C 37 -Sn 43
1.27 0.63 0.025	
67. LP (4)Cl 34	/228. BD*(1) C 29 -Sn 41
1.47 0.59 0.026	
67. LP (4)Cl 34	/232. BD*(1) C 32 -Sn 42
4.16 0.62 0.046	
67. LP (4)Cl 34	/234. BD*(1) C 37 -Sn 43
1.27 0.63 0.025	
67. LP (4)Cl 34	/237. BD*(1)Sn 41 - S 44
3.49 0.55 0.040	
67. LP (4)Cl 34	/238. BD*(1)Sn 41 - S 45
3.20 0.56 0.038	
67. LP (4)Cl 34	/239. BD*(1)Sn 41 - S 47
10.75 0.58 0.072	
67. LP (4)Cl 34	/240. BD*(1)Sn 42 - S 44
5.27 0.56 0.049	
67. LP (4)Cl 34	/241. BD*(1)Sn 42 - S 46
7.77 0.55 0.059	
67. LP (4)Cl 34	/242. BD*(1)Sn 42 - S 49
20.73 0.58 0.099	
67. LP (4)Cl 34	/243. BD*(1)Sn 43 - S 45
2.58 0.56 0.034	
67. LP (4)Cl 34	/244. BD*(1)Sn 43 - S 46
4.42 0.55 0.044	
67. LP (4)Cl 34	/245. BD*(1)Sn 43 - S 51
10.59 0.58 0.071	

Table S4. Atomic coordinates of the optimized structure of $[\text{Me}_3\text{Sn}_3\text{Cl}_3(\text{S})_2(\text{SH})_3]^-$

Sr. No	Atomic No.		Atomic coordinates		
1	6	0	-2.984807	-1.984848	-1.693658
2	50	0	-3.193174	-0.644350	-0.099078
3	16	0	-1.478412	0.019605	1.366054
4	50	0	-0.018282	1.273415	-0.018489
5	16	0	1.864401	1.024296	2.069425
6	17	0	-4.354192	-1.991335	1.502058
7	16	0	-4.866051	0.925783	-0.342482
8	16	0	1.425415	0.000125	-1.405243
9	50	0	3.148921	-0.644165	0.042112
10	17	0	4.279824	-1.971356	-1.597980
11	6	0	0.179893	3.761780	0.232200
12	17	0	-1.732888	1.177113	-1.917352
13	16	0	4.789466	0.987619	0.208099
14	6	0	3.298382	-2.197725	2.006340
15	1	0	4.714338	1.727421	-0.735287
16	1	0	-4.892511	1.636324	0.623681
17	1	0	0.897441	4.143627	-0.492534
18	1	0	-0.791438	4.222593	0.058744
19	1	0	0.519700	3.999248	1.239206
20	1	0	4.316385	-2.196979	2.393108
21	1	0	2.613896	-1.864982	2.785238
22	1	0	3.029741	-3.205570	1.693289
23	1	0	-3.943519	-2.102539	-2.196590
24	1	0	-2.250008	-1.598914	-2.398673
25	1	0	-2.652508	-2.950371	-1.315153
26	1	0	1.570627	1.505891	2.740460

References:

- ¹ A $\nu_{\text{S-H}}$ peak is usually observed between 2500 and 2600 cm^{-1} both in organic thiols and metal hydrosulfides. These peaks are always of low intensity and may go undetected in some cases (For example, please see G. R. Clark, K. R. Flower, W. R. Roper, L. J. Wright, *Organometallics*. 1993, 12, 3810-3811)
- ² SAINT+, 6.02 ed., Bruker AXS, Madison, WI, 1999
- ³ G.M. Sheldrick, SHELX 97, Program for Crystal Structure Refinement from Diffraction Data, University of Göttingen, 1997.
- ⁴ L.J. Farrugia, *J. Appl. Cryst.* 1999, **32**, 837.
- ⁵ J.R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J.M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari,

Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, J. B. G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford CT, 2004

⁶ D. C. Young, Computational chemistry. A practical guide for applying techniques, John Wiley, 2001, pp.100-101.