Supplementary Material

A new six-coordinate organotin(IV) complex of $OP[NC_5H_{10}]_3$: a comparison with an analogous five-coordinate complex by means of X-ray crystallography, Hirshfeld surface analysis and DFT calculations

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Hirshfeld surface analysis:

The survey Hirshfeld surfaces show that H…H contacts in both **1** and **IZOVIE** are majority in the intermolecular interactions covering 90.8% and 75.9% of the total HS, respectively, where visible red spots on the HS of **1** are related to these H…H interactions while for **IZOVIE** not any red spot on the surface is found for such interactions. These H…H contacts are recognized by the points spread out in the center of FP providing the closest contacts. For **1**, these closest contacts are manifested by a short sharp spike on the diagonal plot. Moreover, color change from blue to green in the regions of $d_e = d_i$ (≈ 1.0 – 1.7 Å for **1** and 1.2 – 1.7 Å for **IZOVIE**) on the plot diagonal indicates an increase of the occurrence frequency for H…H contacts.

Besides the H…H contacts, the presence of intermolecular interactions of type C—H…Cl in the crystal structures is evident by the H…Cl/Cl…H FPs which comprise 9.1% of the total HS for **1** and 23.0% for **IZOVIE** (for example: C10—H10B…Cl2, C10…Cl2 = 3.821 (2) Å, ∠C10–H10B–Cl2 = 152.8° and symmetry code: $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ in **IZOVIE**). The related regions on HSs are represented as points in the regions of bottom right ($d_e < d_i$, Cl…H) and top left ($d_e > d_i$, H…Cl) on the corresponding plots. For **IZOVIE**, these regions are characterized as two wings with sharp tips, including some points scattered in the center of plot.

As mentioned above, in **1**, red spots on the HS are only related to H…H contacts, whereas for **IZOVIE**, only two large red spot are visible on the HS which can be assigned to Sn…Cl/Cl…Sn contacts (Sn1…Cl2 = 3.2799 (6) Å; symmetry code: $-x + 1, -y + 1, -z$) with a characteristic shape as two thin boomerangs that are symmetric with respect to the diagonal of the plot in the

Sn…Cl/Cl…Sn FP (figure 4). These contacts include minimum $d_i + d_e$ value of about 3.3 Å which comprises 1.0% of the entire HS.

Vibrational analysis

For **1**, the highest experimental wavenumbers at 2962 cm^{-1} (calculated in the range 3187 cm^{-1} to 3197 cm^{-1}) and 2847 cm^{-1} (calculated: 3069 and 3070 cm^{-1}) are assigned to C—H asymmetric and symmetric stretching vibrational modes for CH_3 group in the $Cl_2Sn(CH_3)_2$ group, respectively. The wavenumbers 2918 cm^{-1} and 2768 cm^{-1} correspond to the same modes for CH_2 groups in the piperidine rings with theoretical values in the range 2982 cm^{-1} to 3147 cm^{-1}. The bending (scissoring) modes are observed at 1452 cm^{-1} for CH_2 groups and at 1354 cm^{-1} (asymmetric mode) and 1233 cm^{-1} (symmetric) for CH_3 groups. This assignment is supported by the theoretical results in the range 1500 cm^{-1} to 1554 cm^{-1} for CH_2 and in the range 1484 to 1495 cm^{-1} (asymmetric) and 1265, 1266, 1275 cm^{-1} (symmetric) for CH_3. The CH_2 bending vibrational modes in the piperidine rings including wagging (experimental: 1304 cm^{-1}, calculated: in the range 1372 cm^{-1} to 1422 cm^{-1}), twisting (experimental: 1259 cm^{-1}, calculated: 1292 cm^{-1} to 1357 cm^{-1}) and rocking (experimental: 1157 cm^{-1}, calculated: 1152 cm^{-1} to 1191 cm^{-1}) are observable. However, the medium (m) or weak (w) bands in 870 (m), 783 (m) and 613 (w) cm^{-1} for the CH_2 rocking modes are also observed besides the strong band at 1157 cm^{-1}. The experimental frequency for the stretching vibrational mode of P═O bond is 1115 cm^{-1} compared to the theoretical value at 1001 cm^{-1}. The various stretching and bending vibrational modes relative to the piperidine rings are found in the range 916 cm^{-1} to 1136 cm^{-1} appearing as five bands in IR spectrum (table 4) which are confirmed by the calculated values in the range 915 cm^{-1} to 1147 cm^{-1}. The PN stretching vibrational modes besides the stretching modes of rings appear as a strong band at 964 cm^{-1} and a medium band at 731 cm^{-1} supported by the calculated data in the range 952 cm^{-1} to 964 cm^{-1} (for the former) and 634 cm^{-1} to 698 cm^{-1} (for the latter). A medium strong band at 845 cm^{-1} represents the vibrational rocking mode of CH_3 groups corresponding to the calculated values in the range 836 to 865 cm^{-1}. The medium strong

bands at 575 cm^{-1} (calculated: 562 cm^{-1}) and 498 cm^{-1} (calculated: 491 cm^{-1}) point to asymmetric and symmetric stretching vibrations of the Sn—C bonds, respectively. The ring deformation mode at 478 cm^{-1} (calculated: 450 cm^{-1}) as a medium band is as well distinguishable in the experimental IR spectrum.

As is seen in table 4, for **IZOVIE** similar calculated results are obtained in which the number of the calculated frequencies is halved relative to **1** as is expected by the presence of only one ligand in **IZOVIE** versus two in **1**.

Table S1. Vibrational assignments of experimental FT-IR frequencies of **1** along with corresponding theoretical vibrational data (cm^{-1}) at B3LYP/SDD level for **1** and **IZOVIE**.

Experimental* (FT-IR, cm^{-1})	Calculated	Calculated	Tentative assignment**
1	**1**	**IZOVIE**	
2962 (s)	3197, 3196, 3188, 3187	3199, 3198, 3170, 3149	Asym. CH Str. of CH_3 groups (of $Cl_2Sn(CH_3)_2$ segment)
2918 (s)	3147 to 3084 (30 frequencies)	3149 to 3092 (15 frequencies)	Asym. CH Str. of CH_2 groups (of rings)
2847 (s)	3070, 3069	3065, 3064	Sym. CH Str. of CH_3 groups
2768 (s)	3063 to 2982 (30 frequencies)	3056 to 2982 (15 frequencies)	Sym. CH Str. of CH_2 groups
1452 (s)	1554 to 1500 (30 frequencies)	1534 to 1501 (15 frequencies)	CH_2 Sciss. in rings
1354 (m)	1495, 1494, 1487, 1484	1493, 1488, 1487, 1484	Asym. CH_3 Sciss. in $Cl_2Sn(CH_3)_2$ segment
1304 (m)	1422 to 1372 (30 frequencies)	1428 to 1377 (15 frequencies)	CH_2 Wagg. in rings
1259 (s)	1357 to 1292 (6 frequencies)	1314, 1306, 1297	CH_2 Twist. in rings
1233 (w)	1275, 1266, 1265	1292, 1291, 1284	Sym. CH_3 Sciss. in $Cl_2Sn(CH_3)_2$ segment
1157 (s)	1191 to 1152 (6 frequencies)	1193, 1192, 1185	CH_2 Rock. in rings
1136 (m)	1147 to 1132 (6 frequencies)	1148, 1144, 1138	CC Str. + CN Str. in rings
1115 (s)	1001	1001	P═O Str.
1097 (s)	1121 to 1095 (6 frequencies)	1107, 1105, 1102	CN Str. + CCH Bend. in rings
1068 (w)	1094 to 1075 (6 frequencies)	1084, 1079, 1073	CC Str. + CNC Bend. + CCH Bend. in rings
964 (s)	964 to 952 (6 frequencies)	962, 958, 948	PN Str. + CC and CN Str. in rings
916 (m)	919 to 915 (6 frequencies)	918, 912, 911	CC Str. + CCH Bend. in rings
870 (m)	898 to 878 (6 frequencies)	873, 871, 870	CH_2 Rock. in rings
845 (m)	865 to 836 (6 frequencies)	863, 851, 832	CH_3 Rock. in $Cl_2Sn(CH_3)_2$ segment
783 (m)	832 to 785 (6 frequencies)	831, 828, 826	CH_2 Rock. in rings
731 (m)	698 to 634 (6 frequencies)	703, 697, 643	PN Str. + CN Str. in rings
613 (w)	571, 570	560	CH_2 Rock. in rings
575 (m)	562	552	Asym. Sn–C Str.
498 (m)	491	506	Sym. Sn–C Str.
478 (m)	450	462	Ring def.

*s: strong; m: medium; w: weak. **Sym.: symmetric; Asym.: asymmetric; Str.: stretching; Sciss.: Scissoring; Bend.: bending; Wagg.: wagging; Ring def.: ring deformation; Rock.: rocking; Twist.: twisting.

Table S2. Experimental isotropic ^{1}H and ^{13}C-NMR chemical shifts for **1** and calculated values for **1** and **IZOVIE** in DMSO solvent on the HF/SDD/DGDZVP level.

1		**IZOVIE**	
Experimental	Calculated	Calculated	Assignment
^{1}H-NMR			
1.05 (s)	0.460, 0.634, 0.724	0.5412, 0.622, 0.650, 0.656, 0.673, 0.713	H atoms of $2CH_3$
3.00 (m)	1.451, 1.639, 1.645, 1.647, 1.654, 1.764	1.332, 1.418, 1.452, 1.714, 1.773, 1.785	H_{para} atoms of NC_5H_{10} rings
3.51 (m)	1.439, 1.465, 1.573, 1.602, 1.639, 1.649, 1.671, 1.674, 1.685, 1.702, 1.711, 1.749	1.351, 1.372, 1.385, 1.399, 1.404, 1.409, 1.512, 1.522, 1.538, 1.542, 1.559, 1.827	H_{meta} atoms of NC_5H_{10} rings
3.77 (m)	2.682, 2.697, 2.745, 2.788, 3.815, 2.849, 2.899, 2.925, 3.092, 3.293, 3.407, 3.597	2.414, 2.427, 2.475, 2.535, 2.581, 2.687, 2.762, 2.764, 2.799, 3.030, 3.439, 3.499	H_{ortho} atoms of NC_5H_{10} rings
^{13}C-NMR			
25.33 (s)	24.455	13.315, 13.688	C atoms of Sn—CH_3
34.60 (s)	26.590, 26.710, 32.593	32.002, 32.035, 32.377	C_{para}, atoms of NC_5H_{10} rings
43.35 (s)	29.500, 29.982, 30.662	33.609, 33.709, 34.413	C_{meta} atoms of NC_5H_{10} rings
45.15 (s)	30.750, 34.331, 34.910	35.130, 35.169, 35.235	C_{meta} atoms of NC_5H_{10} rings
63.95 (s)	45.070, 45.789, 46.817	49.204, 49.515, 49.722	C_{ortho} atoms of NC_5H_{10} rings
67.03 (s)	46.826, 50.105, 50.537	50.321, 50.658, 52.739	C_{ortho} atoms of NC_5H_{10} rings