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# A new six-coordinate organotin(IV) complex of OP[NC<sub>5</sub>H<sub>10</sub>]<sub>3</sub>: A comparison with an analogous five-coordinate complex by means of X-ray crystallography, Hirshfeld surface analysis and DFT calculations

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A new six-coordinate organotin(IV)-phosphoric triamide complex of  $OP(NC_5H_{10})_3 = OP$  was synthesized ( $[Cl_2Sn(CH_3)_2(OP)_2]$ , 1) and characterized by X-ray crystallography and spectroscopic methods (FT-IR, UV-Visible and <sup>1</sup>H/<sup>13</sup>C/<sup>31</sup>P-NMR). The crystal structures of **1** and the analogous previously reported five-coordinate complex  $[Cl_2Sn(CH_3)_2(OP)]$  (IZOVIE) were compared on a structural level and by computational means using Hirshfeld surface analysis, density functional theory (DFT) calculations and the Atom In Molecule (AIM) method. The investigation of intermolecular interactions in the crystal structures of the two complexes by the Hirshfeld surface method indicates that in the absence of normal hydrogen bonds, the chlorine-based interactions H...Cl/Cl., H (for 1 and IZOVIE) and Cl...Sn/Sn...Cl (for **IZOVIE**) play a determinant role in the molecular assemblies. However, the prominent contacts are of H...H type. From calculated electronic parameters such as bond order, Mulliken charge and electron delocalization energy, it was found that the Sn-OP contact has a lower strength in **IZOVIE** than in 1, suggesting a more ionic character of the metal-oxygen contact in fivecoordinate complex IZOVIE. Furthermore, we discuss the similarities and differences of the two complexes 1 and IZOVIE derived from the same ligand OP by density functional theory calculations to present an insight into the organotin(IV)-phosphoric triamide coordination chemistry affected by different geometries and coordination numbers.

*Keywords*: Organotin(IV)-phosphoric triamide complex; X-ray Crystallography; Hirshfeld surface analysis; DFT Calculation; Spectroscopic study

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#### 1. Introduction

Phosphoramide compounds with O=P-N segments have a great potential for usage as *O*-donor ligands in the preparation of metal coordination compounds. In recent years, the attention for especially phosphoramide-based organotin(IV) complexes has increased because of the various applications of these complexes in the pharmaceutical industry [1-4] and agriculture [5, 6]. Among these compounds, the use of the O=P[-N]<sub>3</sub>-based phosphoric triamide (PO) ligand as a subclass of phosphoramides have attracted significant attention for novel syntheses of coordination compounds [7, 8]. Crystal structures of many such complexes have been reported (CSD, Version 5.38, Feb. 2017 update, [9]) which indicate five- and mainly six-coordinate geometries. However, there have been no previous reports of both five- and six-coordinate complexes prepared from the same PO ligand. Moreover, the focus of experimental and computational researches are extended in different areas of chemistry such as the ones mentioned above which can provide the appropriate information of different structural, electronic and spectroscopic aspects. These studies can be useful for investigation and comparison of analogous compounds.

In this paper, we present the synthesis and crystal structure of a new six-coordinate  $Sn^{IV}$  phosphoric triamide complex ([Cl<sub>2</sub>Sn(CH<sub>3</sub>)<sub>2</sub>(OP)<sub>2</sub>] (1) prepared using water-soluble tris(piperidin-1-yl)phosphine oxide (OP(NC<sub>5</sub>H<sub>10</sub>)<sub>3</sub> = OP) ligand and compare it to the crystal structure of a five-coordinate complex [Cl<sub>2</sub>Sn(CH<sub>3</sub>)<sub>2</sub>(OP)] (**IZOVIE**) with the same ligand previously (scheme 1) [10]. Hirshfeld surface analysis [11] and other computational methods are employed to analyze the interactions in 1 and **IZOVIE**.

# 2. Experimental

# 2.1. Materials and measurements

All chemicals were of analytical grade, obtained from commercial sources and used without purification. The infrared (IR) spectrum was recorded on a Bruker ALPHA FT-IR spectrometer using KBr disks. UV-Vis spectrum was recorded on a Shimadzu UV-1650 PC spectrophotometer. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance DR X500 spectrometer. <sup>1</sup>H/<sup>13</sup>C and <sup>31</sup>P chemical shifts were determined relative to TMS and 85% H<sub>3</sub>PO<sub>4</sub>, respectively, as external standards.

# 2.2. Syntheses

For the preparation of ligand  $OP(NC_5H_{10})_3$ , a solution of amine(piperidine) in dry acetonitrile was added dropwise to a solution of  $P(O)Cl_3$  in the same solvent (6:1 molar ratio) at 273 K. After stirring for 4 h, the solvent was removed and the crude product was used in complex reactions.

**2.2.1.** Syntheses of *trans*-dichloro-trans-dimethyl-trans-bis[tris(piperidine-1-yl)phosphine oxide- $\kappa$ O]tin(IV), [Cl<sub>2</sub>Sn(CH<sub>3</sub>)<sub>2</sub>{OP(NC<sub>5</sub>H<sub>10</sub>)<sub>3</sub>}<sub>2</sub>] (1). A solution of [Cl<sub>2</sub>Sn(CH<sub>3</sub>)<sub>2</sub>] (1 mmol) in acetonitrile (5 ml) was added dropwise to an excess of ligand solution (2.5 mmo) in methanol (15 ml). The clear solution was stirred under reflux for 24 h. Colorless crystals were obtained after a few days at room temperature. Yield: 60%. IR (KBr, cm<sup>-1</sup>): 2962, 2918, 2847, 2768, 1452, 1354, 1304, 1259, 1233, 1157, 1136, 1115, 1097, 1068, 964, 916, 870, 845, 783, 731, 613, 575, 498, 478. <sup>1</sup>H NMR (500.13 MHz, DMSO-*d*<sub>6</sub>, 298.0 K, TMS),  $\delta$ (ppm): 1.05 (s, 6H, 2CH<sub>3</sub>, <sup>2</sup>*J*(<sup>119</sup>Sn,H) = 115.0 Hz and <sup>2</sup>*J*(<sup>117</sup>Sn,H)=135.0 Hz [satellites]), 3.00 (m, 12H, NC<sub>5</sub>H<sub>10</sub> ring), 3.51 (m, 24H, NC<sub>5</sub>H<sub>10</sub> ring), 3.77 (m, 24H, NC<sub>5</sub>H<sub>10</sub> ring). <sup>13</sup>C NMR (125.76 MHz, DMSO-*d*<sub>6</sub>, 298.0 K, TMS),  $\delta$ (ppm): 25.33 (s, 2C, Sn-CH<sub>3</sub>), 34.60 (s, 6C, NC<sub>5</sub>H<sub>10</sub> ring), 43.25 (s, 6C, NC<sub>5</sub>H<sub>10</sub> ring), 45.15 (s, 6C, NC<sub>5</sub>H<sub>10</sub> ring), 63.95 (s, 6C, NC<sub>5</sub>H<sub>10</sub> ring), 67.03 (s, 6C, NC<sub>5</sub>H<sub>10</sub> ring). <sup>31</sup>P {<sup>1</sup>H} NMR (202.45 MHz, DMSO-*d*<sub>6</sub>, 298.0 K, 85% H<sub>3</sub>PO<sub>4</sub>),  $\delta$ (ppm): 28.82 (s).

## 2.3. X-ray measurements

A suitable single-crystal for compound **1** was selected for the X-ray diffraction experiment and mounted in a Teflon cryo loop. Details of crystal data and structure refinement are provided in table 1.

Measurements were made on a Gemini diffractometer with a Sapphire3 detector and graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.7107$  Å). The data were corrected for absorption with *CrysAlisPro* [12]. The structure was solved using the charge-flipping method implemented in the *Superflip* program [13] and refined using the *CRYSTALS* program [14]. Non-H atoms were refined anisotropically. The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C-H in the range 0.93-

0.98 Å and  $U_{iso}(H)$  in the range 1.2-1.5 times  $U_{eq}$  of the parent atom). After which the positions were refined with riding constraints [15].

The piperidine rings in one of the PO ligands appeared to be disordered. The disorder was modelled with split positions. Two orientations of the piperidine rings were found, and they were restrained to have a similar geometry. In addition, restraints were used in order to keep reasonable C-C  $sp^3$ - $sp^3$  bond lengths. The anisotropic atomic displacement parameters of adjacent atoms in the disordered fragment were restrained to be the same [16].

*PLATON* [17] and *Mercury* [18] programs were used for making the ORTEP and packing diagrams, respectively.

#### 2.4. Hirshfeld surface analysis

3D Hirshfeld surfaces (HSs) of **1** and **IZOVIE** were generated using *CrystalExplorer* 17.5 [19]. The bond lengths to hydrogen atoms were automatically set to standard neutron values (C-H =

1.083 Å) for calculations. The normalized contact distances  $d_{norm}$  ( = -+-,  $d_e$  and  $d_i$  being the distances from the point to the nearest nucleus external and internal to the surface, respectively), based on van der Waals radii [20], were mapped into the HSs. These surfaces display a simple red-white-blue color scheme for an easy comparison of intermolecular contacts relative to van der Waals radii. Where red spots exhibit short contacts (with distances shorter than the sum of van der Waals radii), white areas represent contacts with distances equal to the sum of the van der Waals radii, and blue regions are free of any close contacts [21].

The HS fingerprint plots (FPs) [22] were constructed from the pair distance  $d_e$ ,  $d_i$  for each individual surface spot displayed on the graph axes. In these plots, the frequency of occurrence of interactions (the number of points with a given  $(d_e,d_i)$  pair) are represented by the different colors blue (low frequency), green (medium) and red (high). Moreover, the  $(d_e > d_i)$  and  $(d_e < d_i)$  regions are displayed on the FPs as complementary regions where one molecule acts as donor  $(d_e > d_i)$  and the other as an acceptor  $(d_e < d_i)$  [23]. These quoted regions are introduced by the reciprocal *X*...H/H...*X* contacts in which *X* atom is located inside (for *X*...H/ $d_e < d_i$ ) or outside (for H...*X*/ $d_e > d_i$ ) the generated HS as an H-atom acceptor.

For **1**, two separate HS analyses were performed for the structure with each orientation of the piperidine ring. Both orientations appeared to have very similar interaction contributions within 0.8% and therefore only one orientation was further analyzed as being fully occupied.

#### 2.5. Computational details

All calculations were performed by density functional theory (DFT) in the Gaussian09 program package [24]. The combined 6-311++G(d,pd) (for C, H, N, O, P and Cl atoms [25]) and LANL2DZ (for Sn atom [26]) basis sets (designed as SDD) were used for all calculations. Starting geometries for calculations were taken from the X-ray crystal structures with neutron based carbon to hydrogen distances. The structures were fully optimized and characterized as true minima by the absence of imaginary frequencies. Vibrational frequencies were determined to provide an estimation of the zero point vibrational energies (ZPVE). The natural bond orbital (NBO) analysis which suggested by Reed *et al.* [27, 28] was applied to determine the origin of the structural behavior. UV-vis spectra and electronic transitions were computed with the time-dependent DFT (TD-DFT) method at the B3LYP/SDD level. The solvent (CH<sub>3</sub>OH) was considered as a uniform dielectric constant with a dielectric constant of 32.7.

Furthermore, the density functional theory was used to calculate the dipole moment ( $\mu$ ), mean polarizability ( $\alpha$ ) and the total first static hyperpolarizability ( $\beta$ ) in terms of *x*, *y*, *z* components as given by following equations [29]:

where ; and = . The GIAO method was used for calculating the <sup>1</sup>H NMR and <sup>43</sup>C NMR chemical shifts at the HF/SDD/DGDZVP level with dimethylsulfoxide (DMSO) as solvent. The Atom In Molecule (AIM) model [30] was employed for the evaluation of Sn-*OP* contacts in two studied complexes by the calculated topological properties of charge density ( $\rho_{(r)}$ ) and its Laplacian ( $L_{(r)} = -\nabla^2(\rho_{(r)})$ ) summarized by their critical points (CPs), where  $\nabla^2(\rho_{(r)}) < 0$  and  $\nabla^2(\rho_{(r)}) > 0$  reveal the concentration and depletion of the electron density, respectively.

#### 3. Results and discussion

#### 3.1. Structural description

The molecular structure of 1 is shown in figure 1. Selected bond lengths and angles are presented in table 2. The asymmetric unit is composed of one-half of the complete molecule located on a center of inversion. In one of the PO ligands, the piperidine rings are disordered over two sets of sites with refined occupancies of 0.495(4) and 0.505(4).

The Sn coordination geometry in **1** is octahedral with the two phosphoramide ligands in a *trans* position with respect to each other. Two chlorine atoms and two methyl groups separately adopt a *trans* position (figure 1).

The piperidine rings adopt a chair conformation and the P atoms in the ligands adopt a distorted tetrahedral environment. The Sn-O, Sn-Cl and Sn-C bond lengths and the Sn-O-P bond angles of **1** are within the expected values [7, 8].

There is an analogous five-coordinate complex of  $OP(NC_5H_{10})_3$ ,

 $[Cl_2Sn(CH_3)_2 \{OP(C_5H_{10}N)_3\}]$  (**IZOVIE** [10]), in which the tin atom exhibits a distorted trigonal bipyramidal coordination with the axial positions being occupied by one Cl and one phosphoric triamide ligand. Two methyl groups and the other Cl atom of the  $[Cl_2Sn(CH_3)_2]$  segment define the equatorial plane. Moreover, for this complex, the parameter  $\tau$  which represents the percentage distortion from trigonal bipyramidal geometry calculated by the Addison method is about 45%. In the Addison method, the parameter  $\tau$  is defined as  $\tau = - \times 100$ , where  $\varphi$  and  $\theta$  are the two observed basal angles [31].

A comparison of the bond lengths of **1** and **IZOVIE** show that the Sn-C, Sn-Cl and P=O bond lengths are slightly longer in **1** than **IZOVIE**, while the Sn-O bond is longer in **IZOVIE** than in **1**. However, the structures of **1** and **IZOVIE** are determined in different temperatures, 175 K and 100 K, respectively. The most important structural difference between five (**IZOVIE**)- and six (1)-coordinate tin complexes of OP[NC<sub>5</sub>H<sub>10</sub>]<sub>3</sub> is the positions of *cis*-methyl groups and *cis*-chlorine atoms in **IZOVIE** versus *trans* positions in **1**. The assessment of various properties affected by these structural features will be discussed in the next sections.

The bond valence sum (BVS) value for the tin ion in **1** was calculated as 4.096, which is close to the formal oxidation states of Sn<sup>IV</sup>.

No classical hydrogen bond is possible in the crystal structure of **1** because there are not appropriate donors and acceptors for such interactions. Stabilization of **1** is produced *via* some

weak interactions. For example, the intermolecular interactions C61-H612...Cl2 hydrogen bonds (C61...Cl2 = 3.422 (5) Å,  $\angle$ C61-H612-Cl2 =  $115.1^{\circ}$  and symmetry code: -x + -, y + -, -z + -) in the structure form a 2D network parallel to the (-101) plane as shown in figure 2.

#### 3.2. Analysis of intermolecular interactions by HSs and FPs

The Hirshfeld surfaces of 1 and **IZOVIE** are given in figures 3 and 4, showing surfaces that have been mapped over  $d_{\text{norm}}$  along with decomposed fingerprint plots. Table 3 presents the percentage contributions of interactions for 1 and **IZOVIE**.

From the figures, it is realized that the interactions H...H in 1 and Sn...Cl/Cl...Sn in **IZOVIE** represent the closest contacts highlighted as red spots on  $d_{norm}$  surfaces. The related FPs comprise 90.8% (H...H) and 1.0% (Sn...Cl/Cl...Sn) of the total HS, for 1 and **IZOVIE**, respectively. Other considerable interactions are C-H...Cl hydrogen bonds which are evidenced by the H...Cl/Cl...H FPs comprising 9.1% of the total HS for 1 and 23.0% for **IZOVIE**. Moreover, it results from the FPs that the highest proportions of interactions for both structures are observed for H...H contacts which cover a wide range of HS (table 3) marked by the points spread out in the center of FP. For details of the HS analysis, see the Supplementary Material.

In summary, the most important difference observed in the molecular assemblies of the studied structures, caused by the reduction of coordination number from six in 1 to five in **IZOVIE**, is the increased contribution of the chlorine-based interactions in **IZOVIE** (24.0%) comparing to 1 (9.1%). Another difference is the presence of the dipolar Sn...Cl type interactions in five-coordinate complex **IZOVIE** which can be rationalized by a smaller steric hindrance, supported by the presence of only one PO ligand in the structure, and also by the *cis*-orientation of coordinated chlorine atoms with respect to each other.

# 3.3. DFT Calculations

**3.3.1. Geometry optimization.** The geometry of complexes **1** and **IZOVIE** were optimized using the B3LYP method with SDD basis set. Calculated geometrical parameters alongside experimental values are presented in table 2. As can be seen, a good agreement is found between the optimized parameters from the DFT calculations with experimental ones from X-ray crystallography results in both complexes. For **1**, the highest difference is about 0.1 Å in bond lengths and about 2° in bond angles, while in **IZOVIE** for bond lengths the same difference

about 0.1 Å is found, but for the bond angles a discrepancy about 10° is observed for the C1-Sn1-Cl1 angle. Such differences are expected, since the X-ray crystallography results correspond to data that were obtained in the solid state whereas the calculated data are valid for the gaseous state.

**3.3.2. Vibrational analysis.** Vibrational frequencies have been computed for the optimized structures of **1** and **IZOVIE** on the DFT(B3LYP)/SDD level. The calculated (for **1** and **IZOVIE**) and observed (for **1**) FT-IR spectra are shown in figure 5. Experimental and calculated vibrational frequencies are listed in table S1, where the observed bands of **1** are assigned by comparison of calculated and experimental IR spectra with the reported IR spectra of similar compounds [7, 32].

For complex 1, the experimental bands in the range 2700 cm<sup>-1</sup> to 2970 cm<sup>-1</sup> are assigned to C-H stretching vibrational modes of CH<sub>2</sub> (in the piperidine rings) and CH<sub>3</sub> (in the Cl<sub>2</sub>Sn(CH<sub>3</sub>)<sub>2</sub> segment) groups. The peaks in the range 1450 cm<sup>-1</sup> to 1160 cm<sup>-1</sup> are attributed to the different types of vibrational modes scissoring, wagging, twisting and rocking of CH<sub>2</sub> and CH<sub>3</sub> groups. The P=O stretching vibrational mode is found at 1115 cm<sup>-1</sup>. At wavenumbers lower than about 1100 cm<sup>-1</sup>, the stretching, bending and rocking vibrational modes of CH<sub>2</sub> groups in the piperidine rings or the combinations of them can be observed. The stretching vibrational modes of the Sn-C bonds are assigned to the bands at 575 cm<sup>-1</sup> and 498 cm<sup>-1</sup>. Similar calculated results are obtained for **IZOVIE** (table S1). More details of the vibrational analysis are provided in the Supplementary Material.

**3.3.3. UV-vis spectra.** The UV-vis spectrum of **1** in CH<sub>3</sub>OH shows a band at 201 nm (absorbance: 0.310 a.u. = 8.43 eV) that may be assigned to the  $\pi \rightarrow \pi^*$  transition of the P=O unit. The calculated results in the same solvent indicate that the calculated absorption band appears at 202 nm with bond energy of 6.15 eV (orbital excitation: HOMO-7 $\rightarrow$ LUMO, 92% contribution). The calculated wavelength is in good agreement with the experimental value.

For **IZOVIE**, the calculated UV-vis spectrum in CH<sub>3</sub>OH shows an absorption band at 205 nm with bond energy of 6.04 eV (orbital excitation: HOMO-6 $\rightarrow$ LUMO, 71%) and a shoulder at 239 nm with a bond energy of 5.19 eV (orbital excitation: HOMO-2 $\rightarrow$ LUMO, 98%). This band and shoulder may be attributed to a combination of the  $\pi \rightarrow \sigma^*/\pi^*$  (empty tin d orbitals)

transition from Cl or PO ligand to Sn and the  $\pi \rightarrow \pi^*$  transition of the P=O unit. These assignments in both complexes were discussed more extensively in the last section.

**3.3.4. NMR spectral studies.** The experimental (for 1) and theoretical (for 1 and **IZOVIE**) chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR spectra are presented in table S2.

The experimental <sup>1</sup>H NMR spectrum of **1** is composed of four signals appearing as one singlet and three multiplet bands. The singlet signal located at 1.05 ppm is assigned to methyl protons of the  $Cl_2Sn(CH_3)_2$  segment. Around this signal, two pairs of satellites are observed which can be used to evaluate the <sup>2</sup>*J*(<sup>119</sup>Sn,<sup>1</sup>H) and <sup>2</sup>*J*(<sup>117</sup>Sn,<sup>1</sup>H) coupling constants, 115.0 and 135.0 Hz. Three multiplet signals at chemical shifts higher than 3.00 ppm are attributed to protons of  $CH_2$  groups of piperidine rings in para-, meta- and ortho-positions, respectively. In the <sup>13</sup>C NMR spectrum of **1**, the six singlet signals for carbon atoms appear in order of increasing chemicals shift as 2C of segment [ $Cl_2Sn(CH_3)_2$ ] (one signal), and then, para- (one signals), meta-(two signals) and ortho- (two signals) C atoms of rings, respectively.

DFT calculations for NMR study were performed at the B3LYP/SDD level and also using some other levels and basis sets, but the obtained results were not in agreement with the experimental data. The CH<sub>3</sub> carbon signal is calculated at higher chemical shift than some other carbon atoms in the calculated <sup>13</sup>C NMR spectra. Finally, the results obtained at the HF/SDD/DGDZVP level are in fairly good agreement with the experimental chemical shifts which are listed in table S2 and discussed.

The calculated chemical shifts of CH<sub>3</sub> protons are at 0.46, 0.63 and 0.72 ppm for **1** and in the range 0.54-0.72 ppm for **IZOVIE**. The CH<sub>2</sub> protons of the piperidine rings are calculated at higher chemical shifts than the CH<sub>3</sub> protons, in the range 1.45-3.60 ppm for **1** and 1.33-3.50 ppm for **IZOVIE**, for para-, meta- and ortho-positions. The calculated <sup>13</sup>C NMR spectra show signals at 24.45 ppm for **1** and at 13.31 and 13.69 ppm for **IZOVIE** corresponding to CH<sub>3</sub> carbon atoms and at the range 26.59-50.54 ppm for **1** and 32.00-52.74 ppm for **IZOVIE** corresponding to para-, meta- and ortho-carbons. Generally, as seen in table S2, there is a relatively good agreement between the results provided by the experimental and calculated <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1**.

**3.3.5.** Nonlinear optical properties. Among NLO materials, there are some reports of organotin(IV) complexes exhibiting nonlinear optical (NLO) properties [33]. For considering the NLO properties of molecular systems, urea is used as a prototypical molecule with a threshold value for the purpose of comparison.

Table 4 presents the non-linear optical property parameters of **1** and **IZOVIE**. As it is seen, the total static dipole moment ( ) and mean polarizability ( ) are slightly greater for complex **1** than for **IZOVIE**, whereas the first-order hyperpolarizability ( ) is calculated for **IZOVIE** higher than **1**. However, parameters and comparing with the corresponding values for urea (3.8312 Å<sup>3</sup> and 0.3728×10<sup>-30</sup> cm<sup>5</sup>/esu, respectively) are lesser for both complexes. Based on the obtained results, it can be concluded that the studied compounds cannot be a good candidate of NLO materials.

**3.3.6. NBO and NPA analyses.** Natural bond orbital (NBO) analysis provides useful information about intermolecular orbital interactions, in particular charge transfer. Indeed, this method describes the Lewis-like molecular bonding pattern of electron pairs and facilitates the analysis of intra- and intermolecular interactions. Natural population analysis (NPA) gives the electron distribution and Mulliken charges in the molecules that play an important role in electronic properties such as dipole moment and polarizability [34].

We focus here on the evaluation and comparison of Sn-O contacts in 1 and IZOVIE which are affected by the Mulliken charge, bond order, the percentage of bond electron density, hybridization and electron delocalization energy ( $E^2$ ). These parameters are listed in table 5.

The Sn-O bond is slightly stronger in the six-coordinate complex **1** than in the fivecoordinate complex **IZOVIE**. It is supported by the lowest bond order values of other bonds Sn-C and Sn-Cl around tin in the segment  $[Cl_2Sn(CH_3)_2(O)_2]$  (as a result of the higher bond order value for the bond Sn-O) for **1** compared to **IZOVIE**. The values of the Mullikan charges show a similar trend. In **1**, tin is attached to the more electronegative carbon and chlorine atoms and hence has a higher positive value than that in **IZOVIE**, where the negative charge of the oxygen atom is almost the same in both complexes. This supports the slightly stronger Sn-O bond in **1** compared to that in **IZOVIE**.

The calculation of the percentage of bond electron density is also in line with these results. Higher differences between these percentages for the Sn-C and Sn-Cl bonds in the

environment around the tin center  $[(Cl)_2Sn(C)_2(O)_n]$  (n = 1 for **IZOVIE** and 2 for **1**) are found for **1** than for **IZOVIE**, reflecting a higher ionic character of these bonds in **1**. Based on these data, it is predicted that the Sn-O bond in **1** has a lower ionic character than this bond in **IZOVIE**, providing a stronger metal-oxygen bond with a more covalent character. This result is also confirmed by the higher values of  $\rho_{(r)}$  at the bond critical point (BCP) of Sn-O for **1** (1.403 a.u.) comparing to **IZOVIE** (1.298 a.u.) calculated using the Atom In Molecule (AIM) theory ( $L_{(r)} = -4.26 \times 10^{-4}$  a.u. for **1** and  $-4.37 \times 10^{-4}$  a.u for **IZOVIE**).

Finally, according to the electron delocalization energies ( $E^2$ , kcal/mol) presented in table 5, the delocalization of electrons from the lone pairs of oxygen to the antibonding orbitals of Sn<sup>IV</sup> results in a strong interaction of LP O with LP\* Sn in 1 stabilizing the six-coordinate complex by 27.84 (for LP(1) O) and 40.17 (for LP(3) O) kcal/mol, whereas the interaction of LP O with BD\* Sn in **IZOVIE** stabilizes the five-coordinate complex by a maximum energy 16.91 kcal/mol (for LP(1) O). These higher electron delocalization energies for the sixcoordinate complex 1 support the hypothesis of a stronger Sn-O bond in 1 than that in **IZOVIE**.

#### 3.3.7. Analysis of frontier molecular orbitals

 $\omega = -$ 

The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) are the most important orbitals in a molecule and play an effective role in estimating chemical reactivity and physical properties. Energies of HOMO and LUMO in a molecule are used for the determination of global reactivity parameters such as electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ), global softness (S) and global electrophilicity index ( $\omega$ ) (table 6 for 1 and **IZOVIE**) that can be calculated using the following equations [35]:

A molecule with a small frontier orbital gap (energy difference between HOMO and LUMO orbitals) acts as a soft molecule, is more polarizable and has a high chemical reactivity. The calculated values of these parameters are collected in table 6 for 1 and **IZOVIE**. The six-coordinate complex 1 with a higher HOMO–LUMO energy gap is a slightly more stable structure than five-coordinate complex **IZOVIE**, and complex 1 can be identified as a harder molecule with a lower electrophilicity comparing to **IZOVIE**.

Frontier molecular orbitals for **1** and **IZOVIE** are shown in figure 6. In **1**, the HOMO and LUMO orbitals are mainly localized on non-metal atoms (HOMO: 95% on Cl and CH<sub>3</sub> ligands, 4% on PO ligands and LUMO: 32% on Cl and CH<sub>3</sub>, 34% on PO ligands). For **IZOVIE**, the HOMO orbital is mainly localized on non-metal atoms (97% on Cl and CH<sub>3</sub> ligands), while the LUMO orbital is located on metal and non-metal atoms equally (50% on Sn, 40% on Cl and CH<sub>3</sub> ligands). No considerable transfer of electron density is observed between these frontier orbitals for both complexes.

Moreover, in 1 the value of the contribution of the PO ligand in HOMO-7 is equal to 91% and this value is reduced to 34% for LUMO as mentioned above. These data affirm that the transfer HOMO-7 $\rightarrow$ LUMO (observed in the calculated UV-vis spectrum) corresponds to intraligand charge-transfer (ILCT) in the PO ligand; however, based on these data the probability of occurrence of ligand-to-metal charge-transfer (LMCT) cannot be neglected (from the PO ligand to Sn). For **IZOVIE**, in the HOMO-6 orbital, the PO ligand has less than 6% electron population whereas the Cl and CH<sub>3</sub> ligands have about 94% contribution. So, the orbital excitation HOMO-6 $\rightarrow$ LUMO (observed in the calculated UV-vis spectrum) in this complex can be predicted mainly as a LMCT (from Cl ligand to Sn), where the chance of occurrence of ILCT is very low. Moreover, in the HOMO-2 orbital, the electron populations are found to be 97% for the PO ligand and 3% for the Sn metal and the Cl and CH<sub>3</sub> ligands. So, the orbital excitation HOMO-2 $\rightarrow$ LUMO (observed in the calculated UV-vis spectrum) can be predicted as a LMCT (from PO ligand to Sn) with a much lower probability of ILCT.

# 4. Conclusion

The synthesis of a new six-coordinate organotin(IV)-phosphoric triamide complex,  $[Cl_2Sn(CH_3)_2(OP)_2]$  (1), bearing water-soluble phosphoric triamide ligand  $OP(NC_5H_{10})_3 = OP$ and the characterization by spectroscopic and X-ray crystallography methods is reported. This complex and its analogous five-coordinate complex [Cl<sub>2</sub>Sn(CH<sub>3</sub>)<sub>2</sub>(OP)] (**IZOVIE**) have been compared using density functional theory (DFT) and Hirshfeld surface (HS) calculations. The results show similar FT-IR and NMR spectra, but different UV-vis spectra for **1** and **IZOVIE**, and also a slightly stronger Sn-OP interaction in **1** compared to **IZOVIE**, which is supported by the X-ray crystallography. More stability, less electrophilicity and more hardness are found for **1** with a higher HOMO-LUMO energy gap compared to **IZOVIE**. Furthermore, HS analysis reveals that H...H contacts are majority in both structures, whereas H...Cl/Cl...H are more important in **IZOVIE** than in **1** because of less steric hindrance caused by the presence of only one *PO* ligand.

# Supplementary data

CCDC number 1556342 for 1 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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## **Figure captions**

Figure 1. The structure of  $[Cl_2Sn(CH_3)_2\{OP(NC_5H_{10})_3\}_2]$  (1) showing the atom-labeling scheme for non-H atoms. Displacement ellipsoids are given at 50% probability and hydrogen atoms are drawn as small spheres of arbitrary radii.

Figure 2. View of the crystal packing of **1** showing a 2D network generated by C61-H612...Cl2 hydrogen bonds (black dash lines) parallel to the (-101) plane. The Sn<sup>IV</sup> centers and H and Cl contact atoms are highlighted as "balls". Hydrogen atoms not involved in intermolecular interactions are removed for clarity.

Figure 3. Upper: Views of  $d_{norm}$  HS for 1, in two orientations, surrounded by neighboring molecules associated with close contacts H...H (identified as red spots); Lower: Decomposed H...H and H...Cl/Cl...H FPs and related percentage contributions to the total HS area for 1. The full FP (with the range values of 0.8 Å <  $d_e$ ,  $d_i < 2.7$  Å) appears as a grey shadow below each decomposed plot.

Figure 4. View of  $d_{norm}$  HS for **IZOVIE** surrounded by neighboring molecule associated with close contact Cl...Sn/Sn...Cl (identified as red spots). Decomposed H...H, H...Cl/Cl...H and Cl...Sn/Sn...Cl FPs and related percentage contribution to the total HS area are also shown. The full FP (with the range values of  $1.1 \text{ Å} < d_e$ ,  $d_i < 2.4 \text{ Å}$ ) appears as a grey shadow below each decomposed plot.

Figure 5. Calculated (upper) and experimental (lower) FT-IR spectra of 1 and IZOVIE in the range 400-4000 cm<sup>-1</sup>.

Figure 6. Frontier molecular orbital plots for 1 (upper) and IZOVIE (lower).

















Wavenumber (cm<sup>-1</sup>)



V

Empirical formula	$C_{32}H_{65}Cl_{2}N_{6}O_{2}P_{2}Sn$
Formula weight	817.44
Temperature (K)	175
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.5838(1)  Å
	b = 15.3314(1)  Å
	c = 14.0269(1) Å
	$\beta = 91.711(1)^{\circ}$
Volume (Å <sup>3</sup> )	1845.14(3)
Ζ	2
Density (calculated) (g/cm <sup>3</sup> )	1.471
Absorption coefficient (mm <sup>-1</sup> )	0.962
<i>F</i> (000)	858
Crystal size (mm <sup>3</sup> )	$0.30 \times 0.35 \times 0.50$
Crystal color / habit	Colorless / block
Theta range for data collection (°)	1.968 to 37.614
Index ranges	$-14 \le h \le 14$
	$-25 \le k \le 25$
	$-24 \le l \le 24$
Reflections collected	108060
Independent reflections	9569 $[R_{int} = 0.043]$
Absorption correction	multi-scan / CrysAlisPro
Max. and min. transmission	1.00000 and 0.93970
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	9569 / 270 / 377
Goodness-of-fit on $F^2$	0.9044
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0511, wR_2 = 0.1501$
$\sim R$ indices (all data)	$R_1 = 0.0610, wR_2 = 0.1583$
Largest diff. peak and hole (e.Å-3)	1.72 and -1.49

Table 1. Crystal data and structure refinement for compound **1**.

1	Experimental	Calculated	IZOVIE	Experimental	Calculated
Sn1-O3	2.2043 (16)	2.248	Sn1-O1	2.2231 (13)	2.338
Sn1-Cl2	2.5607 (6)	2.673	Sn1-Cl1	2.3890 (5)	2.487
Sn1-Cl2 <sup>i</sup>	2.5607 (6)	2.673	Sn1-Cl2	2.5511 (5)	2.529
Sn1-O3 <sup>i</sup>	2.2043 (16)	2.248	Sn1-C1	2.1067 (19)	2.144
Sn1-C4	2.120 (3)	2.145	Sn1-C2	2.1013 (19)	2.144
Sn1-C4 <sup>i</sup>	2.120 (3)	2.145	P1-O1	1.4900 (14)	1.609
P40-O3	1.514 (4)	1.609	P1-N1	1.6370 (16)	1.716
P41-O3	1.500 (4)	-	P1-N2	1.6433 (16)	1.736
P40-N51	1.642 (5)	1.720	P1-N3	1.6341 (16)	1.715
P40-N171	1.650 (5)	1.724	Cl1-Sn1-O1	86.81 (4)	84.69
P40-N111	1.680 (2)	1.727	Cl2-Sn1-O1 <	178.73 (4)	179.38
P41-N50	1.628 (5)	-	C1-Sn1-O1	86.60 (7)	85.10
P41-N170	1.647 (5)	-	C2-Sn1-O1	85.62 (7)	85.80
P41-N110	1.600 (2)	-	C1-Sn1-Cl1	103.74 (6)	113.99
Cl2 <sup>i</sup> -Sn1-O3	88.67 (6)	90.94	C2-Sn1-Cl1	103.26 (6)	112.24
Cl2 <sup>i</sup> -Sn1-C4	88.67 (9)	88.76	C1-Sn1-C2	151.40 (9)	131.66
O3 <sup>i</sup> -Sn1-C4 <sup>i</sup>	91.90 (10)	93.61	Cl1-Sn1-Cl2	94.187 (18)	95.49
Cl2 <sup>i</sup> -Sn1-Cl2	179.996	180.00	P1-O1-Sn1	159.53 (9)	161.04
O3 <sup>i</sup> -Sn1-Cl2	91.33 (6)	90.94	>		
C4 <sup>i</sup> -Sn1-Cl2	90.33 (9)	88.76			
O3 <sup>i</sup> -Sn1-O3	179.995	180.00			
C4 <sup>i</sup> -Sn1-O3	88.10 (10)	86.39			
P40-O3-Sn1	148.55 (17)	147.45			
P41-O3-Sn1	153.02 (18)	-			

Table 2. Selected calculated and experimental bond distances (Å) and angles (°) for 1 and IZOVIE.

Symmetry transformations used to generate equivalent atoms for 1: (i): -x+1, -y+1, -z+1.

	НН	H Cl / ClH	ClSn/SnCl
1	90.8 (red spots)	9.1	- ^
IZOVIE	75.9	23.0	1.0 (red spots)

Table 3. Summary of the percentage contributions of interactions for 1 and IZOVIE.

Table 4. The calculated electric dipole moments ( $\mu$ ) (a.u.) and total static dipole moment () (Debye), static polarizability components () (a.u.) and mean polarizability () (Å<sup>3</sup>), and first hyperpolarizability components ( $\beta$ ) (a.u.) and first-order hyperpolarizability () (cm<sup>5</sup>/esu) for 1 and IZOVIE at B3LYP/SDD level.

Parameters	1	IZOVIE	Parameters	1	IZOVIE
$\mu_{\rm x}$	-2.788	5.308	$\beta_{\rm xxx}$	3.963	5.057
$\mu_{ m y}$	-4.545	-1.369	$\beta_{\rm xxy}$	3.013	9.603
$\mu_{ m z}$	-7.165	-4.934	$\beta_{\mathrm{xyy}}$	1.547	1.432
	8.931	7.375	$eta_{ m yyy}$	-3.292	-1.276
			$\beta_{ m xxz}$	-1.093	1.217
$\alpha_{\rm xx}$	4.870	2.752	$eta_{ m yyz}$	1.400	-8.015
$\alpha_{ m yy}$	4.500	2.638	$\beta_{ m xzz}$	-8.171	7.125
$\alpha_{zz}$	4.385	2.533	$eta_{ ext{yzz}}$	3.212	1.248
	0.679	0.391	$\beta_{zzz}$	-3.827	-1.249
<				0.046×10 <sup>-30</sup>	0.160×10 <sup>-30</sup>
C	$\sim$				

Atom	Mullik	on abaraa	Pond	Bond		%Bond elec	etron
Atom	IVIUIIIK	en charge	Dolla	order		density	<u> </u>
	1	IZOVIE		1	IZOVIE	1	IZÓVIE
Sn	1.501	1.254	Sn-O	0.200	0.170	-	
0	-	-0.834	Sn-C	0.644	0.697	24.88-	26.08-
	0.855					75.12	73.92
Р	1.715	1.662	Sn-Cl	0.420	0.611	11.53-	17.28-
						88.47	82.72
Cl	-	-0.441, -	Sn-Cl	-	0.557	~~>	14.95-
	0.603	0.495				$\left( \right)$	85.05
C of CH <sub>3</sub>	-	-0.917	P=O	0.954	0.974	26.62-	26.64-
5	0.947	0.921				73.38	73.36
Donor-Ac	ceptor in	teractions					
Compoun	Dono	Hybridizatio	Occupatio	Accepto	Hybridizatio	Occupatio	$E^2$
d	r	n	n number	r	n	n number	 (kcal/mol
				$\sim$			)
1	LP	$Sp^{1.1}$	1.909	LP*(1)	$Sp^1$	0.232	27.84
	(1) O	1	<	Sn	1		
		$Sp^{3.5}$	1.857	LP* (1)	$Sp^1$	0.232	40.17
	(3) O			Sn	ľ		
IZOVIE				$\checkmark$			
	LP	Sp <sup>0.7</sup>	1 909	BD* (1)	$Sn^{8.0}$ - $Sn^{4.8}$	0 144	16 91
	(1) O		$\sim$	Sn-Cl			
	ĹP	Sp <sup>6.0</sup>	1.868	BD* (1)	$Sp^{8.0}$ - $Sp^{4.8}$	0.144	11.78
	(3) O			Sn-Cl			
	(-) -						
	$\bigcirc$	$\leq$					
	(( <b>5</b> )	$\checkmark$					
P							
	))						
$\vee$							

Table 5. Results of NBO and NPA analyses for 1 and **IZOVIE** determined by DFT method at the B3LYP/SDD level.

Parameter	1	IZOVIE
$E_{LUMO}$ - $E_{HOMO}$ (eV)	6.299	6.072
$E_{LUMO} + E_{HOMO} (eV)$	-4.890	-6.831
Electronegativity $(\chi)$	2.445	3.415
Chemical potential $(\mu)$	-2.445	-3.415
Chemical hardness $(\eta)$	3.149	3.036
Softness (S)	0.159	0.165
Electrophilicity index $(\omega)$	0.949	1.921
Sn(CH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>		
SIGCH <sub>32</sub> Cl <sub>2</sub>		

Table 6. Calculated global reactivity descriptors of **1** and **IZOVIE** at the B3LYP/SDD level.