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Structural study, vibrational and optical properties, Hirshfeld surface analysis and DFT investigation of a novel organic cation hexachloridostannate(IV), (C₅H₈N₃)₂[SnCl₆]

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ABSTRACT

In this work, a novel compound bis(2,6-diaminopyridinium) hexachloridostannate(IV), formulated as (C₅H₈N₃)₂[SnCl₆], has been synthesized and characterized by powder and single crystal X-ray diffraction (XRD), IR and UV-Vis spectroscopies, and Hirshfeld surface analysis. The title compound crystallizes in the monoclinic system, *P*2₁/*c* space group with *a* = 7.1481(2) Å, *b* = 11.1164 (3) Å, *c* = 12.4535(1) Å, β = 104.688(4)⁰ and *V* = 957.23(4) Å³. Its crystal structure can be described as an alternation between organic and inorganic columns running along the *a*-axis. The structure is stabilized by N–H...Cl hydrogen bonds and π - π interactions. Hirshfeld surface analysis has been performed to gain insight into the behavior of intermolecular interactions. The powder XRD data confirms the phase purity of the crystalline sample. The calculations were performed using the B3LYP functional and 6-311+G(2d,2p) basis set for H, C, N, Cl and LANL2DZ for Sn. The optical proprieties were investigated by UV-Vis spectroscopy study and the electronic properties HOMO and LUMO energies were calculated by TD-DFT and the CPCM model using methanol as solvent. The nucleophilic and electrophilic binding site regions are elucidated using the molecular electrostatic potential (MEP).

Key words: hexachloridostannate; crystal structure; Hirshfeld surface; IR spectroscopy; gap energy; DFT calculation

1. Introduction

Inorganic chemistry is beginning to have a major impact on medicine. It offers great potential for the design of novel therapeutic and diagnostic agents [1]. Furthermore, the use of metals such as tin in medicine raises a very important issue like toxicity. In addition to the biological evaluation for therapeutic potential, further chemical and pharmacological studies are necessary to unravel a structure–activity relationship for organotin derivatives that can guide subsequent design of new drug candidates [2-4]. Correlation of X-ray crystallographic data with anti-cancer activity has shown interesting results [5-7]. The Sn-X (X: halogen) length as well as the X-Sn-X bond angle seem to play an important role in the development of antitumor activity by octahedral Sn(IV) compounds [8]. While therapeutics-based organotin compounds continue to attract the greatest attention, ‘inorganic’ tin drugs are in or are finding their way into the clinic, being exploited now in treatment of jaundice, cancers and wet Age-related Macular Degeneration (AMD) which is a leading cause of blindness in older adult whereas organotin halides and their complexes with amines and other ligands exhibit borderline activities against P388 and L1210 leukaemia [9-21].

On the other hand, the choice of the ligand has an attractive wide influence in the synthesis of compound based on tin. Diaminopyridine as ligand can offer more benefits in many biologically important molecules such as cytosine derivatives, folates and antifolates drugs. When correlated with its availability with N donor systems including high affinity for metalions. Combination between these two entities leads to the synthesis of new compounds which thanks to their synergistic effect play a key role in control and design of new materials with appropriate and desired properties.

Organic-inorganic hybrids materials received a considerable attention due to their flexibility of these structures which gives a rich and fertile playground for the elaboration of interesting crystal structure with different physical properties. Furthermore, there are many interesting aspects of inorganic and organic tin chemistry; these complexes and their derivatives received considerable attention due to their interesting dielectric properties [22], optoelectronic [23] and development of low-cost photovoltaic devices [24]. It should be noted that tin and its derivatives are in commercial use more than any other elements. Considering the attractive properties a of Sn(IV) and the new promising opportunities that may open with regard to the development of useful organic–inorganic hybrid materials [25], we report in this work the synthesis, and a combined experimental and a theoretical studies of a new hybrid compound namely, bis(2,6-diaminopyridinium) hexachlorostannate(IV). The crystal structure was carried out by single crystal X-ray diffraction and the phase purity of the crystalline sample

was studied by powder X-ray diffraction. Vibrational study by IR spectroscopy and optical properties by UV–Vis diffuse reflectance spectroscopy were done to identify the functional groups present in the studied compound and to determine the band gap respectively. Moreover, DFT calculations were reported in order to carry out correlation between crystal structure and physical properties. Hirshfeld surface analysis and molecular electrostatic potential (MEP) were also performed.

2. Experimental

2.1. Materials and measurements

All reagents and solvents were obtained from commercial sources and used without further purification. The infrared (IR) spectrum was collected on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer with ATR accessory in the range of 4000–400 cm^{-1} using pellets made from a pure crystalline sample. UV-Vis spectrum was recorded on an Ellice SL–164 Double BEAM UV-Vis spectrophotometer in the range 200–800 nm using methanol as solvent.

2.2. Synthesis of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$

SnCl_2 (0.3506 g, 1 mmol) was dissolved in 5ml of MeOH resulting in a transparent solution. HCl (5 mL) was added (solution A). 2,6-diaminopyridine, $\text{C}_5\text{H}_7\text{N}_3$ (0.218 g, 2 mmol), was dissolved in 5mL MeOH resulting in pale yellow solution. HCl (37%, 2 mL) was added, resulting in a colorless solution (solution B). Solution B was added drop wise to solution A and slow solvent evaporation was achieved by covering the solution with perforated parafilm. After three weeks prismatic transparent crystals were present. The colorless crystals later characterized as $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$ will be the subject of a subsequent report. In order to check the purity of the studied phase, X-ray powder diffraction measurement was carried out at room temperature. As shown in Fig. 1, the similarity of the calculated pattern using Mercury program and the experimental one confirms the high purity level of the synthesized phase and confirms the crystal data used indicating that the compound was isolated as a single phase.

2.3. Single-crystal X-ray diffraction

A single crystal was carefully selected under polarizing microscope in order to perform its structural analysis by X-ray diffraction. Diffraction data were collected at 293 K with Enraf–Nonius CAD4 automatic four-circle equipped with graphite monochromator using Mo-K α (λ

= 0.71073 Å) radiation. The structure was solved with direct methods using SHELXT2018/3 [26] refined by full-matrix least squares technique on F^2 through SHELXL2018/3 [27]. The non-hydrogen atoms were refined anisotropically [28, 29]. The C-bonded H atoms were fixed using AFIX 43 instruction. Those attached to nitrogen atoms were also located from difference maps and restrained with $d(\text{N-H})=0.89(1)$ Å applying DFIX instruction. An empirical psi-scan absorption correction was applied ($T_{\min} = 0.81$, $T_{\max} = 0.99$). The final refinement converged to the values of $R(F^2) = 2.8\%$ and $wR(F^2) = 6.9\%$. The molecular plots were drawn with the Diamond 3 program [30]. The basic crystallographic data together with the details of the X-ray measurement and refinement are summarized in Table 1.

2.4. Computational details

The structure was optimized with the Density Functional Theory DFT method using the Gaussian 09 program [31]. The calculations were performed using the B3LYP functional and 6-311+G(2d,2p) basis set for H, C, N, Cl and LANL2DZ for Sn [32-33]. Input geometric structures of these salts are based on the optimum configuration that have been obtained by X-ray software (cif file). Vibrational wavenumbers calculations in the gas phase were then performed at the same level of theory of the optimized geometries to confirm that there are no imaginary wavenumbers. The calculated UV-Vis spectrum was calculated with time-dependent density functional theory TD-DFT and the CPCM model using methanol as solvent [34]. Some electronic properties were also calculated, as well as the graphical representations of HOMO and LUMO. The molecular Hirshfeld surfaces [35] in the crystal structure have been constructed based on the electron distribution calculated as the sum of spherical atom electron densities [36]. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface is unique [37] and it is this property that suggests the possibility of gaining additional intermolecular interactions of molecular crystals. The intermolecular interactions of the title compound are quantified using Hirshfeld surface analysis. This approach is a graphical tool for visualization and understanding of intermolecular interactions. The normalized contact distance (d_{norm}) based on both d_e (the distance from the point to the nearest nucleus external to the surface) and d_i (the distance to the nearest nucleus internal to the surface), and the van der Waals (vdW) radii of the atom, enables identification of the regions of particular importance to intermolecular interactions. The value of the d_{norm} is negative or positive when intermolecular contacts are shorter or longer than vdW separations, respectively. The combination of d_e and d_i in the form of a two-

dimensional (2D) fingerprint plot provides a summary of intermolecular contacts in the crystal. The Hirshfeld surfaces are mapped over d_{norm} and shape index, and 2D fingerprint plots presented in this paper were generated using CrystalExplorer 3.1. Graphical plots of the molecular Hirshfeld surface mapped with d_{norm} used a red, white, blue color scheme, where red highlights shorter contacts, white is used for contacts around the vdW separation, and blue is for longer contacts.

3. Results and discussion

3.1. Crystal structure

(C₅H₈N₃)₂[SnCl₆] crystallizes at room temperature, in the monoclinic system, space group $P2_1/c$ with two formula unit cell ($Z = 2$). The asymmetric unit of the title compound contains one protonated cation (C₅H₈N₃)⁺ and a half of the [SnCl₆]²⁻ anion. Similarly to the previous studies [38-45], the anion lies on the inversion center (Fig.2). This question is probably connected with the octahedral structure of the anion which facilitates formation of the centrosymmetric structure in a self-assembly process. A survey in the Cambridge Structural Database (CSD version 5.40 (November 2018)) revealed that among 179 structures of hexachloridostannate, the [SnCl₆]²⁻ anion lies on the inversion center in 79 cases [46, 47]. The crystal structure of the title compound can be described as an alternation between organic and inorganic anions into columns running along the a -axis (Fig.3). These columns are further extended into 2D mixed layers packed along the [100] direction and parallel to (bc) plan mediated by N–H $\cdots$ Cl hydrogen bonds (Fig. 4). Distances and bond angles involved in hydrogen bonds are presented in Table 2.

The Sn atom was surrounded by six bridging chlorine atoms leading to an octahedral with the Sn-Cl distances are pairwise identical [Sn-Cl1 = Sn-Cl1ⁱ = 2.4248 (6) Å; Sn-Cl2 = Sn-Cl2ⁱ = 2.4350 (8) Å; Sn1-Cl3 = Sn1-Cl3ⁱ = 2.4164 (7) Å] which indicate ideal octahedral geometry (Table 3). A similar configuration of the [SnCl₆]²⁻ anion was also found for (C₆H₅NH₃)₂[SnCl₆] [48]. This SnCl₆ octahedron is ideal with Cl–Sn–Cl bond angles are also normal (89.10 (3)~90.90 (3)°, 179.99 (2)° ~ 180°), which are very close to 90° and 180° for an ideal octahedron. These geometric parameters are similar to the previously published results [49-51]. In this structure, the average values of the distortion parameters of the anion [SnCl₆]²⁻ are calculated using the following equations [38]:

$$ID(\text{Sn-Cl}) = 1/6 (\sum |di - dm|/dm)$$

$$ID(Cl-Sn-Cl) = 1/12 (\sum |a_i - am|/am)$$

where a_i is the (Cl-Sn-Cl) angle, d_i the (Sn-Cl) distance, m the average values and $ID(Sn-Cl)=0.0026$ and $ID(Cl-Sn-Cl)=0.0002$. The low values of the distortion indices indicate that the coordination geometry of the metal is slightly distorted octahedral, this can agree either with the stereochemical inactivity of the $5s^2$ lone pair of Sn(II) or with the absence of the $5s$ electrons in Sn(IV) [52]. The BVS calculation of the Sn ion (BVS = 4.01) confirmed the presumed oxidation state of Sn(IV). On the other hand, the tin octahedra are packed along the a -axis with a separation distance between the nearest $[SnCl_6]^{2-}$ dianions, in this direction, being 7.1481 Å which corresponds to the a parameter value. The cohesion between hexachloridostannate(IV) anions is provided by Cl...Cl interactions. In addition, the shortest distance between chlorine atoms of the nearest $[SnCl_6]^{2-}$ entities is 3.691 Å along a -axis. Furthermore, the $SnCl_6$ octahedra form chains along the $[001]$ direction where the shortest Cl...Cl separation is about 3.793 Å (Fig.5). This Cl...Cl interaction is sufficient to ensure the cohesion within these chains. Such halogen-halogen contacts are known to create weak antiferromagnetic interactions [53].

Concerning the organic part, it was formed by one type of cation 2,6-diaminopyridinium. Within the protonated amine molecule, the C-C and N-C distances range, from 1.366 (5) Å to 1.376 (6) Å and from 1.334(4) Å to 1.355(4) Å, respectively. The C-N-C angle is equal to 124.5(3)°. Therefore, the pyridinium cations always possess an expanded angle of C-N-C [53] in comparison with the parent pyridine [116.94 (3)°], which confirm well that protonation takes place on the pyridine ring N atom. The selected bond distances and angles are illustrated in Table 2. Corresponding interatomic bond lengths and angles in the two independent cations of the structural unit of the title compound are similar to those obtained in other 2,6-diaminopyridinium salts such as [54-56]. As it can be seen clearly from Fig. 6, the two neighboring anti-parallel organic cations are linked together through the aromatic-aromatic interactions with a distance 3.8368 (1) Å of π - π interactions between two pyridine rings and stacked each other by turns in a face to face mode to form columns along the a -axis.

3.2. Vibrational study

To gain more information on the functional groups present in the crystal, we have investigated the infrared absorption at room temperature. Superposed theoretical and experimental crystal IR are presented in Figure 7. In the IR absorption spectrum, the dynamics of the $-NH_2$ group in the 2,6-diaminopyridinium cation predicts the presence of several and dispersed vibrational

normal modes due to their participation in several hydrogen bonds types. Their IR bands are observed at 3320-3398-3418 cm^{-1} which assigned as NH_2 symmetric stretching vibrations. The corresponding calculated values appear as several peaks in the 3326-3385 cm^{-1} region. Similarly, the NH_2 asymmetric mode is observed at 3575 cm^{-1} which is theoretically predicted at 3562 cm^{-1} . The NH_2 scissoring vibration mode $\delta(\text{NH}_2)$ is at 1643 cm^{-1} , theoretically, this mode is predicted at 1636 cm^{-1} as a strong band. Moreover, the stretching vibration $\nu(\text{NH}^+)$ has been identified at 3261 cm^{-1} in the IR spectrum and its theoretical band is located at 3241 cm^{-1} . Furthermore, the stretching vibrations $\nu(\text{C-H})$ are observed at many wavenumbers in the 3091-3202 cm^{-1} region. Theoretically, these bands are noticed at 3070-3149 cm^{-1} region. On the other side, the stretching vibration for $\nu(\text{C=N})$, $\nu(\text{C-C})$ and $\nu(\text{C-N})$ are observed in the range 1171-1610 cm^{-1} . The theoretical counterparts of these bands appear at 1159-1604 cm^{-1} region. The bands observed between 530-1106 cm^{-1} are ascribed to $\nu(\text{C=N-C})$, $\nu(\text{C=C-C})$, $\nu(\text{C-C=N})$ [53, 57, 58] which is theoretically predicted at 536-1106 cm^{-1} region. The absorption band identified at 1296 cm^{-1} can be assigned to $\nu(\text{C-NH}_2)$ [53], the corresponding theoretical value is located at 1302 cm^{-1} . According to previous works containing the hexachlorostannate anion, the internal vibrational modes of $[\text{SnCl}_6]^{2-}$ anion appear below 500 cm^{-1} in IR spectrum. DFT calculations showed also that the inorganic entities lead to vibrations below 500 cm^{-1} . In this case, to attribute the infrared spectrum, we only focused on the vibrations of 2,6-diaminopyridinium cation. The most intense IR absorption bands observed and calculated wavenumbers assigned to $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$ are regrouped in Table 4.

The experimental single crystal IR spectrum of the studied compound is in good agreement with the calculated one. Thus, the precision is well-sufficient to assign the experimental wavenumbers and to confirm the attributions proposed above. Fig.8 shows a linear correlation of the experimental and calculated IR spectra. All theoretical bands placed within this range (400–4000 cm^{-1}) show a good linear correlation with the experimental wavenumbers with a correlation factor (R^2) of 0.976. A little difference between the theoretical and experimental values may be attributed to intermolecular interaction in the solid state which is obviously absent in the calculations and is due to the fact that the theoretical calculation was carried in the gas phase whereas the experimental one was determined in solid state.

According to the literature, the isolated $[\text{SnCl}_6]^{2-}$ anion possesses ideally O_h symmetry and, thus, will have six fundamental vibrations: $\nu_1(\text{A}_{1g}, 311 \text{ cm}^{-1})$, $\nu_2(\text{E}_g, 229 \text{ cm}^{-1})$, $\nu_3(\text{F}_{1u}, 303$

cm^{-1}), ν_4 (F_{1g} , 166 cm^{-1}), ν_5 (F_{2g} , 158 cm^{-1}) and ν_6 (F_{2u} , inactive). Of these, F_{1u} and F_{1g} are infrared active, while A_{1g} , E_g and F_{2g} are Raman active. The F_{2u} is inactive [59-62].

3.3. Optical properties

To study the electronic absorption of the title compound, the UV-vis spectrum is carried out. To compare the experimentally obtained spectra with theoretical values, TD-DFT method and CPCM model using methanol as solvent were applied to obtain a prediction of the electronic spectra. Simulated UV spectrum bandwidth was 2685.83 cm^{-1} (0.333 eV). Both the experimental and theoretical electronic absorption spectra were measured in methanol solution and recorded within the range 200-600 nm (Fig.9). The experimental UV-Vis spectrum of the studied compound displays clearly two absorption bands related to the conjugated system. The lower wavelength at 242 nm was ascribed to the $\pi-\pi^*$ transition which is theoretically predicted at 247 nm [63-66] while the strong absorption peak at 332 nm (calculated at 349 nm) was assigned to the $n-\pi^*$ absorption bands of the 2,6-diaminopyridinium [53]. Infact, the direct and indirect optical band gap energy of the title compound can be calculated by simply plotting $(\alpha h\nu)^2$ versus $(h\nu)$ and $(\alpha h\nu)^{1/2}$ versus $(h\nu)$, according to the Tauc relation [67]:

$$\alpha h\nu = B (h\nu - E_g)^{1/2}$$

where α is the absorption coefficient, $h\nu$ is the photon energy of the incident photon, E_g is the direct band gap energy, and B is a constant. The absorption coefficient (α) was determined using a relation deduced from Beer-Lambert's relation, $\alpha = 2.303A/d$, where d value is 1.0 cm and A is the absorbance determined from the UV-Vis spectrum. The gap energy is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$ as shown in Fig. 10. Thus, the estimated optical band gap is about 4.402 eV. This large band gap value indicates that the grown crystal possesses a dielectric behavior that induces polarization when powerful radiation is incident on the material. The most important frontier molecular orbitals (FMOs) such as HOMO and LUMO play a crucial part in the chemical stability of the molecule [68]. The HOMO represents the ability to donate an electron and the LUMO represents the ability to accept an electron. The energy gap between HOMO and LUMO also determines the chemical reactivity, optical polarizability, chemical hardness and explains the charge transfer interaction that takes place within the molecule [69]. The HOMO-LUMO

energy gap $E_g=4.482$ eV is large (Fig. 11), implies a high kinetic stability and a low chemical reactivity, because it is energetically unfavorable to add electron to LUMO and extract the electrons from HOMO [68].

3.4. Hirshfeld surface analysis

The Hirshfeld surfaces of the title compound, mapped over d_{norm} and shape index are shown in Fig. 12. The red spots on the around of the d_{norm} surface are attributed to the N-H...Cl, hydrogen bonds which show the closest intermolecular interactions in the compound. In the shape-index map (Fig. 12b), the adjacent red and blue triangle-like patches show concave regions that indicate π - π stacking interactions.

The 2D fingerprint plots can be deconstructed to highlight particular atom pair contacts. The contributions from different interaction types which overlap in the full fingerprint are then separated (Fig. 13a). The H...Cl/Cl...H interactions attributed to the N-H...Cl hydrogen bonds are the most abundant interactions (52.3%); which contributes to stability of the title compound stability (Fig. 13b). Fig. 13c shows that the next most important interaction surface is H...H interactions (17.7%); these electrostatic interactions are also an important contributor to the crystal stability. The C...H/H...C contact (11.5%) constitutes the third interaction present on the Hirshfeld surface (Fig. 13d). Fig. 13e shows the N...H/H...N interactions (8.4%). On the other hand, the C...C contact in fingerprint plots (3.7%, Fig.13f), appears as a tower like shape with the equal d_e and d_i ($d_e = d_i = 1.7 \text{ \AA}$) give us information about aromatic donor-acceptor interactions [53]. The other interactions constitute 6.4% of the Hirshfeld surface.

The molecular electrostatic potential (MEP) has been used as a qualitative tool for identifying molecular regions susceptible to electrophilic or nucleophilic attack, and for analyzing and predicting noncovalent interactions [70-73]. The electrostatic potential maps are color-coded and are subdivided into many regions where those various colors are used to identify different potentials. Intermediate potentials are assigned colors according to the following color spectrum: red < orange < yellow < green < blue. Based on this scheme, we can usually identify red regions of a map as being the most electron rich regions of a molecule, blue regions of a map as being the most electron-poor regions, whereas the green color signifies

the neutral electrostatic potential. As can be seen from the electrostatic potential map shown on Fig. 14, the most negative potential red colored is mainly localized in electronegative chlorine of $[\text{SnCl}_6]^{2-}$. Where blue associated to the maximum positive region indicates the strongest attraction. However, the region with maximum positive potential blue colored is localized on the H atoms of $-\text{NH}_2$ group, which can be considered as possible sites for nucleophilic attack. According to these results, we can say that there is a global electrostatic attraction between the $[\text{SnCl}_6]^{2-}$ anions and the organic cations which adds up to the favorable N-H...Cl hydrogen bonds.

Fig. 15 shows the voids in the crystal structure of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$. These are based on the sum of spherical atomic electron densities at the appropriate nuclear positions (procrystal electron density). The crystal voids calculation (results under 0.002 a.u. isovalue) shows the void volume of title compound to be of the order of $70.54 \text{ \AA}^3$ and surface area in the order of $295.40 \text{ \AA}^2$. With the porosity, the calculated void volume of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$ is 7.37%. There are no large cavities. We note that the electron-density isosurfaces are not completely closed around the components, but are open at those locations where interspecies approaches are found, e.g. N-H...Cl

4. Conclusion

Good quality single crystals of a novel organic-inorganic hybrid compound $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$ has been successfully synthesized by slow evaporation method at room temperature. This compound belongs to the monoclinic system with the $P2_1/c$ space group. The crystal structure can be described as a 2D mixed organic-inorganic layers packed along the [100] direction and parallel to (bc) plan. The cohesion and the stability result from the establishment of N-H...Cl hydrogen bonds between the organic cations and inorganic anions. Investigation of intermolecular interactions and crystal packing *via* Hirshfeld surface analysis reveals that H...Cl/Cl...H (52.3%) and H...H (17.7%) intermolecular interactions are the most abundant in the crystal structure. The vibrational absorption bands were identified by infrared spectroscopy. The optical properties were investigated and the energy gap of this material was found to be at 4.402 eV. DFT calculations allow the attribution of the experimental bands in IR and UV-visible spectra. Hence, this compound has good relationship consistency between the experimental and theoretical studies. Furthermore, HOMO-LUMO energy gap has been computed using quantum chemical computations to get an insight into the compound. The molecular electrostatic potential (MEP) shows that the nucleophile site is distributed around

the chlorine atoms due to the intermolecular N—H...Cl interactions; in the molecular structure it indicates the strongest repulsion site (electrophilic attack), whereas the strongest attraction regions (nucleophilic attack) portrayed by the blue spots are localized on the hydrogen atoms of -NH_2 group.

Supplementary Material

Cif file containing complete information about the structure of this studied hybrid compound was deposited with the Cambridge Crystallographic Data Center (CCDC1827642); the file is freely available upon request from the following website:

http://www.ccdc.cam.ac.uk/data_request/cif

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Table 1. Crystallographic data for $(C_5H_8N_3)_2[SnCl_6]$

Empirical formula	$(C_5H_8N_3)_2[SnCl_6]$
Formula weight ($g\ mol^{-1}$)	551.68
Temperature (K)	293
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	7.1481 (2)
b (Å), $\beta(^{\circ})$	11.1164 (3), 104.688 (4)
c (Å)	12.4535 (1)
Z	2
V (Å ³)	957.23 (4)
Density calculated ($Mg\ m^{-3}$)	1.914
Independent parameters	126
Range for data collection	$\theta_{min} = 2.5^{\circ}$, $\theta_{max} = 27.0^{\circ}$
Absorption coefficient (mm^{-1})	2.177
$F(000)$	540
Reflections collected - Independent	3237-2079

R_{int} - $R(F^2)$ [$I > 2\sigma(I)$]- $wR(F^2)$	0.038, 0.024, 0.054
S(GOF)	1.081

Table 2. Selected bond distances and angles in $(C_5H_8N_3)_2[SnCl_6]$

Organic cation $(C_5H_8N_3)^+$		
Distances (Å)		
	Experimental	Theoretical
C1—C2	1.370 (5)	1.387
C1—C4	1.369 (4)	1.386
C2—C3	1.375 (6)	1.394
C4—C5	1.376 (5)	1.396
N1—C3	1.356 (4)	1.361
N1—C5	1.352 (4)	1.361
N2—C5	1.335 (4)	1.347
N3—C3	1.340 (5)	1.348
Average relative error = 0.0098		Root-mean-square error (RMSE) = 0.0143
Angles(°)		
C1—C2—C3	118.7 (3)	118.5
C1—C4—C5	118.7 (3)	118.6
C4—C1—C2	122.4 (3)	122.1
C5—N1—C3	124.4 (3)	124.2
N1—C3—C2	117.8 (3)	118.4
N1—C5—C4	117.9 (3)	118.1
N2—C5—N1	117.9 (3)	117.1
N2—C5—C4	124.2 (3)	124.7
N3—C3—N1	116.6 (4)	116.8
N3—C3—C2	125.5 (3)	124.6

Average relative error = 0.0008		Root-mean-square error (RMSE) = 0.4816	
Inorganic anion [SnCl ₆] ²⁻			
Distances (Å)			
	Experimental	Theoretical	
Distances (Å)			
Sn—Cl1	2.4248 (6)	2.4584	
Sn—Cl1 ¹	2.4248 (6)	2.4730	
Sn—Cl2 ¹	2.4350 (8)	2.3685	
Sn—Cl3	2.4164 (7)	2.4240	
Sn—Cl3 ¹	2.4164 (7)	2.4230	
Average relative error = 0.0024		Root-mean-square error(RMSE) = 0.04	
Angles(°)			
Cl1—Sn—Cl2	90.16 (3)	85.1271	
Cl1—Sn—Cl2 ¹	89.84 (3)	95.1907	
Cl1i—Sn—Cl2	89.84 (3)	84.9437	
Cl1i—Sn—Cl2 ¹	90.17 (3)	94.6248	
Cl3—Sn—Cl2	89.10 (3)	85.8111	
Cl3—Sn—Cl1	90.32 (2)	91.5876	
Cl3—Sn—Cl1 ¹	89.68 (2)	90.2223	
Cl3i—Sn—Cl1 ¹	90.32 (2)	87.9045	
Cl3i—Sn—Cl1	89.69 (2)	88.5263	
Cl3i—Sn—Cl2	90.90 (3)	83.9694	
Cl3i—Sn—Cl2 ¹	89.10 (3)	93.6639	
Cl3—Sn—Cl2 ¹	90.90 (3)	96.5487	
Average relative error =0.0064		Root-mean-square error (RMSE) =3.6161	

Symmetry codes: (i) -x, -y+1, -z+1.

Table 3. Main interatomic distances (Å) and bond angles (°) involved in hydrogen bonds

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H8...Cl2	0.88 (1)	2.53 (2)	3.278 (3)	143 (3)
N2—H7...Cl1	0.89 (1)	2.63 (1)	3.489 (3)	164 (3)
N2—H6...Cl1 ⁱ	0.89 (1)	2.84 (2)	3.675 (3)	157 (4)
N2—H6...Cl3 ⁱⁱ	0.89 (1)	2.81 (5)	3.302 (3)	117 (4)
N3—H3...Cl2 ⁱⁱⁱ	0.89 (1)	2.70 (3)	3.446 (3)	142 (4)

Symmetry codes : (i) -x, y-1/2, -z+1/2 ; (ii) x, -y+1/2, z-1/2 ; (iii) x, -y+1/2, z+1/2

Table 4. IR observed and calculated w (cm⁻¹)
And assignment for (C₅H₈N₃)₂[SnCl₆]

ν (cm ⁻¹)	Experimental	Calculated
$\nu(\text{NH}_2)_{\text{sym}}$	3418-3398-3320	3385, 3379, 3326
$\nu(\text{NH}_2)_{\text{asym}}$	3575	3562
$\delta(\text{NH}_2)$	1643	1636
$\nu(\text{NH}^+)$	3261	3241
$\nu(\text{CH})$	3202-3091	3149-3070
$\nu(\text{C=H}), \nu(\text{C=N})$ $\nu(\text{C-C}), \nu(\text{C-N})$	1610-1171	1604-1159
$\nu(\text{C=N-C}), \nu(\text{C=C-C}),$ $\nu(\text{C-C=N})$	1106-530	1106-536
$\nu(\text{C-NH}_2)$	1296	1302

Fig. 1. Calculated and experimental powder XRD patterns of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$

Fig.2. The asymmetric unit of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$, showing the atom numbering scheme.
Displacement ellipsoids are drawn at the 50% probability level.

Fig.3. Perspective view of the crystal structure of $(C_5H_8N_3)_2[SnCl_6]$, showing the alternation between organic and inorganic anions into columns running along the a -axis.

Fig.4. 2D hydrogen-bonded supramolecular network present in $(C_5H_8N_3)_2[SnCl_6]$ formed by mixed organic-inorganic layers parallel to (bc) plan linked by N-H...Cl hydrogen bonds

Fig. 5. $\text{Cl}\cdots\text{Cl}$ interactions between the nearest $[\text{SnCl}_6]^{2-}$ anions along a and c axes.

Fig. 6. Perspective view of the crystal structure of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$, showing the arrangement of 2,6-diaminopyridinium into columns running along the a -axis (left) and the π - π interactions between two pyridine rings (right). The hydrogen atoms have been omitted for clarity.

Fig.7. Calculated and experimental IR absorption spectrum of $(C_5H_8N_3)_2[SnCl_6]$

Fig. 8. The fit between the experimental and calculated IR data for $(C_5H_8N_3)_2[SnCl_6]$

Fig. 9. The experimental and theoretical UV visible spectra of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$

Fig. 10. Tauc Plots of $(F(R) hv)^{1/2}$ versus energy of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$

Fig.11. Molecular orbital surfaces for the HOMO and LUMO of $(C_5H_8N_3)_2[SnCl_6]$

Fig. 12. 3D Hirshfeld surfaces of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$ mapped over d_{norm} (a) and shape-index (b). The surface is shown as transparent to allow visualization of the orientation and conformation of the functional groups.

Fig. 13. The 2D fingerprint plots of $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{SnCl}_6]$: all (a) and resolved into $\text{H}\cdots\text{Cl}/\text{H}\cdots\text{Cl}$ (b), $\text{H}\cdots\text{H}$ (c), $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ (d), $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ (e) and $\text{C}\cdots\text{C}$ (f) contacts showing the percentages participations to the total Hirshfeld surface area.

Fig.14. Molecular electrostatic potential map of (C₅H₈N₃)₂[SnCl₆]

Fig.15. Void plot in the crystal structure of (C₅H₈N₃)₂[SnCl₆]

Highlights

- A new hybrid compound was synthesized by slow evaporation at room temperature.
- The atomic arrangement shows alternation of inorganic and organic columns.
- The crystal packing is insured by N-H...Cl hydrogen bonds and π - π interactions.
- DFT calculations were reported in order to carry out correlation between crystal structure and physical properties.