



ORIGINAL ARTICLE

Amine adduct with tin (II) chloride: Synthesis, molecular structure characterization, and DFT computational studies



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Abstract The reaction of the tetramethylethylenediamine [(CH₃)₂NCH₂CH₂N(CH₃)₂] with SnCl₂ in toluene provided the adduct dichloro-(1,2-bis(dimethylamino)ethane-*N,N'*)-tin(II) with a tetracoordinate metal center and *pseudo*-trigonal bipyramidal geometry with a stereochemically active unshared electron pair in its vertex. This compound was characterized by IR, NMR (¹H, ¹³C, and ¹¹⁹Sn) and X-ray studies. The X-ray crystal structure of tin(II) complex shows just one of these three possible isomers. The relative energies of the three different isomers, HOMO and LUMO orbitals, and NMR chemical shifts were calculated, using the density functional theory in order to determine the coordination number.

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1. Introduction

There is widespread interest in the chemistry of divalent derivatives of heavier analogues of carbenes i.e., stannylenes, feature an electrodeficient with six electrons in the valence shell (Mizuhata et al., 2009; Dias et al., 1998; Ayers et al., 2001). Based on the stannylenes electronic structure can lead to amphiphilic behavior, and these are capable of forming complexes with Lewis bases and also yield adduct with Lewis acids due to the empty “*p*” orbital and the free lone pair, respectively (Veith and Recktenwald, 1982; Shiryayev and Mironov, 1983; Gehrhus et al., 1996; Gehrhus and Lappert, 1998; Haaf et al., 2000; Nagendran and Roesky, 2008; Asay et al., 2011; Zabula and Hahn, 2008; Dias and Ayers, 2002) Fig. 1. Stable tin(II) compounds

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of formula (SnR_2) and (RSnX_1) (R = bulky ligand, X = halide) are well-characterized. In contrast, derivatives of tin(II) of the type $\text{Sn}(\text{L}_2)\text{R}$, where L_2 is a small ligand, have received much less attention. To the best of our knowledge, only few such compounds are known, and structural data are available for [$\text{SnCl}_2\cdot 2(1\text{-vinylimidazole})$] (Sergei et al., 1990), [$\text{SnBrCl}(\text{THF})_2$] (Janiak et al., 1997), each of which contains Sn(II) in a highly distorted “T” tetrahedral environment. Divalent tin compounds are promising molecules in organic synthesis and synthesis of new materials (Kavara et al., 2008), by acting as ligands for transition metals (Hahn et al., 2008), and activators of carbon dioxide (Ferro et al., 2011). Specifically, the tin(II) complexes can act as catalysts in the synthesis of biodiesel (Cardoso et al., 2009), and polymerization of rac-Lactide (Dove et al., 2001, 2006; Nimitsiriwat et al., 2008).

On the other hand, we have been interested in the synthesis of tin (II) complexes derived from ligands with electrodonor atoms such as NN or NO (Jiménez-Pérez et al., 2008; Ibarra-Rodríguez et al., 2012; Muñoz-Flores et al., 2012). Thus, continuing with our research, herein we report on the preparation of tin (II) complex adduct with TMEDA which has been more stable at room temperature and air due to the formation of a five-membered ring (chelate effect). It has been characterized by single-crystal X-ray structural analysis and theoretical calculations.

2. Experimental

2.1. Material and equipments

All the manipulations were performed under an inert gas atmosphere of dried nitrogen in standard Schlenk glassware. Toluene was dried according to the known procedures and saturated with N_2 . All starting materials were purchased from Aldrich Chemical Company. Solvents were used without further purification. Melting points were performed on an Electrothermal Mel-Temp apparatus and are uncorrected. Infrared spectrum (KBr pellets) of solid sample was recorded on Perkin Elmer 1600 FT-IR spectrophotometer. ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded in $(\text{CD}_3)_2\text{SO}$ on a Bruker advance DPX 400: ^1H (399.78 MHz), ^{13}C (100.52 MHz) and ^{119}Sn (149.8 MHz). Chemical shifts (ppm) are relative to $(\text{CH}_3)_4\text{Si}$ for ^1H and ^{13}C and to $(\text{CH}_3)_4\text{Sn}$ for ^{119}Sn .

2.2. Crystal structure determination

The crystal of **1** was covered with a layer of hydrocarbon oil that was selected and mounted with paratone-N oil on a cryo-loop, and immediately placed in the low-temperature nitrogen stream at 100(2) K. The data for **1** were recorded on a Bruker SMART APEX CCD area detector system

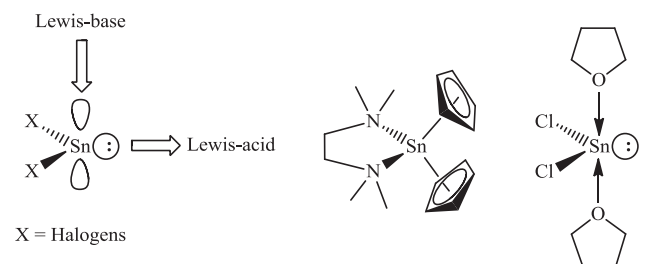


Fig. 1 Probable bonding of stannylenes with Lewis bases and acids and some adducts.

equipped with an Oxford Cryosystems 700 Series Cryostream cooler, a graphite monochromator, and a Mo $\text{K}\alpha$ fine-focus sealed tube ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using SHELXS-97 (Sheldrick, 1990) and refined against F^2 on all data by full-matrix least-squares with SHELXL-97 (Sheldrick, 1997). All of the software manipulations were done under the WIN-GX environment program set (Farrugia, 1999). All heavier atoms were found by Fourier map difference and refined anisotropically. Some hydrogen atoms were found by Fourier map differences and refined isotropically. The remaining hydrogen atoms were geometrically modeled and are not refined. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Centre: CCDC 1521362.

2.3. Synthesis of compound 1

A solution of SnCl_2 (0.4 g, 2.12 mmol) in toluene was added tetramethylethylenediamine (0.37 g, 3.19 mmol) at room temperature with stirring for 18 h. After this time, a precipitated was isolated as white solid in 61% yield (0.4 g). After stirring the solvent, it was reduced *in vacuum* to 20% and then it was cooled at -20°C , after two days the crystallized compound. Mp. 240°C . FTIR (KBr) cm^{-1} : 3010, 2958 (C—H), 1482, 986 (C—N). ^1H NMR (399.78 MHz, $\text{DMSO}-d_6$) $\delta = 2.71$ (s, CH_2 , 4H), 2.46 (s, CH_3 , 12H). ^{13}C NMR (100.52 MHz, $\text{DMSO}-d_6$) $\delta = 53.95$ (CH_2 , 2C), 45.78 (CH_3 , 4C). ^{119}Sn NMR (149.8 MHz, $\text{DMSO}-d_6$) $\delta = -161.4$ ppm, $\Delta\nu_{1/2} = 3840$ Hz.

2.4. Computational details

The geometry of all structures **1(a-c)** and **2** was fully optimized with the Perdew-Burke-Ernzerhof (PBE) (Perdew et al., 1996, 1997) functional in combination with the def2-TZVPP basis set (Weigend and Ahlrichs, 2005), using the GAUSSIAN 09 software package (Frisch et al., 2009). Their vibrational frequencies were calculated with the same level of theory. ^{119}Sn NMR calculations were carried out to quantify the chemical shifts in structures **1(a-c)**, using the Gauge-Independent Atomic Orbital (GIAO) at the same level of theory. The reference molecule $(\text{CH}_3)_4\text{Sn}$ was also optimized and its isotropic NMR shielding constants were calculated using the same method. The PCM method was used to calculate all structures in toluene for bulk solvent effects. The Results were visualized using the Chemcraft program v1.7.

3. Results and discussion

3.1. Synthesis and characterization of compound 1

Reaction of tetramethylethylenediamine (TMEDA) with SnCl_2 in toluene provided the tin adduct **1** (Scheme S1) in acceptable yields as a colorless sharp melting crystalline material with good solubility in organic solvent as THF, ether, chloroform and present low solubility in non-polar solvents, and it was stable at air and room temperature. The room temperature ^{119}Sn NMR spectra of compound **1** (S1), in deuterated dimethylsulfoxide ($\text{DMSO}-d_6$), exhibit only one resonance at $\delta = -161.4$ ppm ($\Delta\nu_{1/2} = 3840$ Hz), which

indicates a tetracoordinate tin atom. Interestingly, the broad signal exhibits a probable dynamic behavior between tetracoordinate and tricoordinate tin atom as previously has been reported (Hsu and Geanagel, 1980) Fig. 2. However, crystal structure supports a tetracoordinate tin atom. ^1H NMR (399.78 MHz) spectra of **1** taken at 298 K showed that both signals of methyl and methylene groups are shifted to high frequencies (2.71, 2.46 ppm) which indicates the $\text{N} \rightarrow \text{Sn}$ coordination bonds (see S4).

3.2. X-ray structure

Compound **1** crystallized in the orthorhombic space group $P2_12_12_1$ as a monomer and in the unit cell there are four molecules. Details of the X-ray crystallographic data are in Table 1. Value of the N1-Sn bond length (2.397 Å) is less than N2-Sn (2.585 Å), and these values are higher than those compared to the molecule reported by Archer et al., 1987. [N1-Sn (2.43 Å), N2-Sn (2.36 Å)]. The N1-Sn-N2 angle value is 78.9° due to the formation of a five-membered heterocyclic; this behavior is typical for cyclic stannylenes and it is in good agreement with values reported for similar molecules (Braunschweig et al., 1995). The crystal structure shows only one isomer of three possible (see Figs. 3 and S2) where the metal center (Sn) is four-coordinated. The geometry of the tin atom is *pseudo*-bipyramidal: Cl1 and N1 atoms are in the apical positions, and Cl2 and N2 are in the equatorial positions; the electron pair is localized on the tin atom. The sum of angles around the tin atom is 325.65° [N2-Sn-Cl1 (83.82°), Cl1-Sn-Cl2 (86.14°), Cl2-Sn-N1 (82.84°), N1-Sn-N2 (72.85°)] and the lone pair or electrons at tin possesses high *s*-character.

Molecule **1** displays intermolecular interactions of the tin atom and chlorine atom with distance of 3.624 Å, which is less than the Van der Waals radii. The interaction of two adjacent molecules with Sn and Cl atoms forms a zig-zag polymer chain as shown in (S3), reported by the similar GeCl_2 complex (Cheng et al., 2010).

3.3. Theoretical calculations

In order to learn more in detail the electron and structural behavior of compound **1**, we have explored its potential energy surface. Three conformers were found (Fig. 4) using the density functional theory. The PBE/def2-TZVPP method suggests that the most stable isomer belongs to structure **1b**, this structure is very similar to conformer **1a**, and the only difference is the orientation of both chlorine atoms. The energy difference is

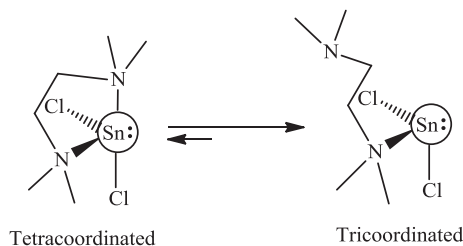


Fig. 2 Possible dynamic behavior of tin complex in solution.

Table 1 Selected bond lengths (Å) and angles ($^\circ$) for $[\text{SnCl}_2\text{-TMEDA}]$.

Sn-N(1)	2.397(2)	Sn-Cl(1)	2.4817(7)
Sn-N(2)	2.585(2)	Sn-Cl(2)	2.6739(7)
N(1)-N(2)	2.961(29)		
N(1)-Sn-N(2)	72.85 (7)	Cl(1)-Sn-Cl(2)	86.14 (2)
N(1)-Sn-Cl(1)	96.87 (5)	N(2)-Sn-Cl(1)	83.82 (5)
N(1)-Sn-Cl(2)	82.84 (5)	N(2)-Sn-Cl(2)	152.29 (5)
Calculated (1a) by PBE/def2-TZVPP method			
Sn-N(1)	2.52	Sn-Cl(1)	2.88
Sn-N(2)	2.82	Sn-Cl(2)	2.54
N(1)-N(2)	3.09		
N(1)-Sn-N(2)	70.3	Cl(1)-Sn-Cl(2)	93.0
N(1)-Sn-Cl(1)	93.8	N(2)-Sn-Cl(1)	82.4
N(1)-Sn-Cl(2)	85.8	N(2)-Sn-Cl(2)	155.1

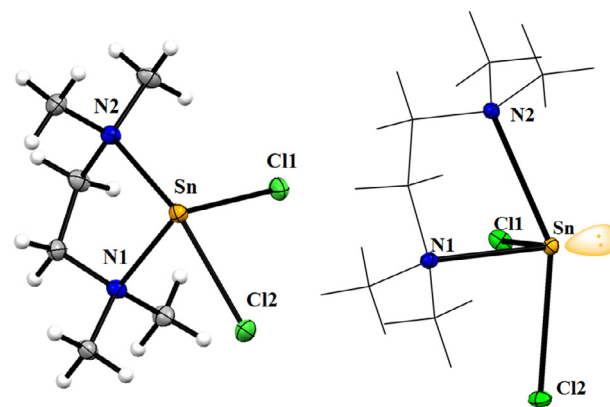


Fig. 3 X-ray structure of tin compound. Ellipsoids are drawn at the 50% probability level.

only 0.18 kcal/mol in gas phase, while in toluene is 0.17 kcal/mol. Interestingly, the structure that has been crystallized is the number **1a** (labeled as **1** in Fig. 3). However, as seen in Fig. 4, both structures can readily inter-convert between them. In Table 1, we can see some distances and angles calculated in order to be compared with those obtained in X-ray structure. The calculated conversion barrier between **1a** and **1b** is 11.59 kcal/mol in gas phase, while in toluene this value is slightly lower, 10.41 kcal/mol. With these energetic results we can say that both structures may simultaneously exist in solution and crystallize in similar conditions. Furthermore, we calculated the HOMO orbitals for the three structures in order to locate the direction of the free electron density on the tin atom. Fig. 5 clearly shows the orientation of that lone pair. On the other hand, we have also calculated the NMR chemical shifts for the tin atom. It is very likely that one DMSO molecule in solution is coordinated with the tin atom (Fig. 6). The calculated chemical shift value for that penta-coordinated tin is -144.1 ppm. The experimental chemical shift value is -161.4 ppm, and this is slightly higher ($\Delta\delta = 17.3$ ppm) than the computed one. The calculated value for the tetra-coordinated structure **1b** is 38.2 ppm.

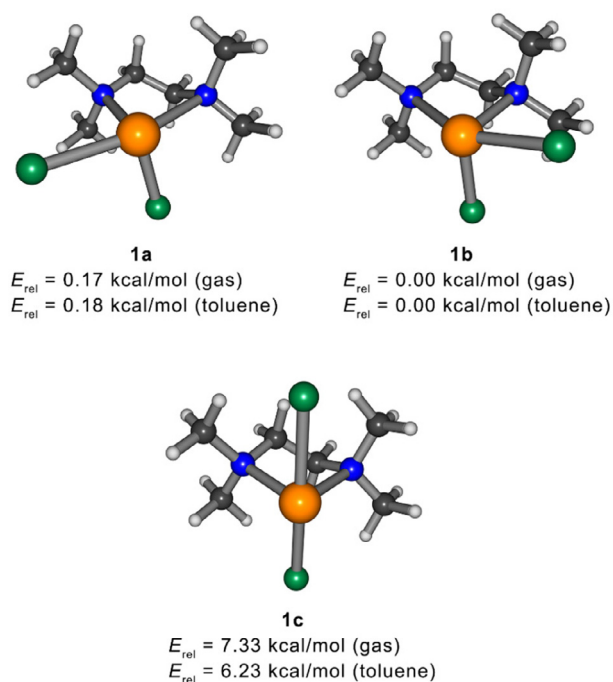


Fig. 4 Relative energies for tin structures, computed at the PBE/def2-TZVPP level of theory, in gas and liquid phases, using the PCM method.

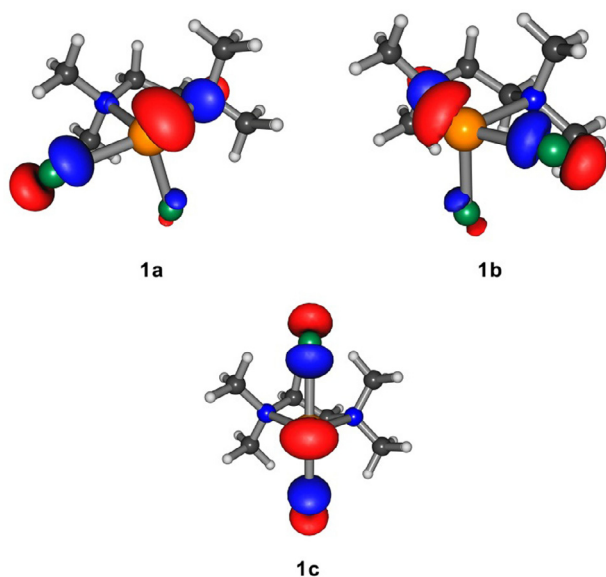


Fig. 5 HOMO orbitals for structures **1 a-c**, using a contour value of 0.08.

4. Conclusions

In summary, we describe the synthesis, characterization in solution, solid state and gas phase of the $\text{SnCl}_2\text{TMEDA}$ monomeric adduct. Solution **1** exhibits a probable dynamic behavior between a tetracoordinate and a tricoordinate tin atom. X-ray and theoretical calculations are in good agreement with the most stable conformers. The energy values calculated for **1a** and **1b** are very similar and are almost zero,

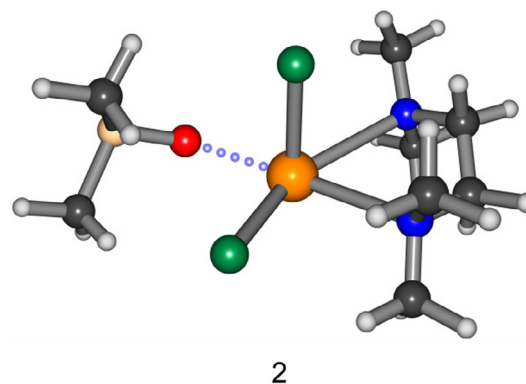


Fig. 6 Tin structures pentacoordinated with DMSO (**2**).

so we can say that both conformers are possible in solution. This energy difference is negligible and can be attributed to the method used.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2016.12.006>.

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