



Dedicated to Professor Valer Farcasan
on the occasion of his 95th anniversary

NOTE

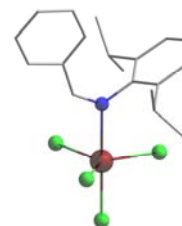
MOLECULAR STRUCTURE OF $[\text{SnCl}_4(\text{N}=\text{CH}-\text{C}_6\text{H}_5)(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)]$, A TIN TETRACHLORIDE COMPLEX WITH AN (IMINO)ARYL LIGAND

Ioana BARBUL and Richard Attila VARGA*

Supramolecular Organic and Organometallic Chemistry Centre (CCSOOM), Chemistry Department, Faculty of Chemistry
and Chemical Engineering, Babes-Bolyai University, RO-400028 Cluj-Napoca, Roumania

Received January 15, 2015

The title compound $[\text{SnCl}_4(\text{N}=\text{CH}-\text{C}_6\text{H}_5)(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)]$, obtained from the reaction of tin tetrachloride with the (imino)aryl ligand $(\text{N}=\text{CH}-\text{C}_6\text{H}_5)(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$, was investigated by single crystal X-ray diffraction. The metal atom has a slightly distorted trigonal bipyramidal geometry as result of a strong $\text{N} \rightarrow \text{Sn}$ interaction.



INTRODUCTION

Several complexes of SnCl_4 with nitrogen containing ligands, *i. e.* $[\text{SnCl}_4(\text{RCN})_2]$ ($\text{R} = \text{Me}$, Et , ^iPr , C_6H_{11} , C_7H_7),¹ $[\text{SnCl}_4(\text{C}_{16}\text{H}_6\text{N}_6)]$,² $[\text{SnCl}_4(\text{Ph}_2\text{PS}_2\text{N}_3)_2]$,³ $[\text{SnCl}_4\{(\text{N}=\text{CH}-\text{C}_6\text{H}_5)(4\text{-Cl})\text{C}_6\text{H}_3\}_2]$,⁴ $[\text{SnCl}_4(\text{C}_{12}\text{H}_8\text{N}_2)]$,⁵ $[\text{SnCl}_4(\text{C}_2\text{H}_7\text{N})_2]$,⁶ were investigated by means of single crystal X-ray diffraction. In all cases the metal atom is hexacoordinated with octahedral coordination geometry, the nitrogen atoms of the ligand(s) situated either in *cis* or *trans* positions. Only one example, $[\text{SnCl}_4(\text{C}_7\text{H}_{13}\text{N})]$,⁷ of pentacoordinated tin atom in tin tetrachloride N-donor ligand adduct was reported so far. On the other hand, our interest in (imino)aryltin(IV) species⁸ drove us to investigate the *orto*-metallation of Schiff's bases by SnCl_4 , as reported by Clegg and colab.⁹

RESULTS AND DISCUSSION

The reaction of (*E*)-*N*-(2,6-diisopropylphenyl)-1-phenylmethanimine with SnCl_4 , in a 4:3 molar ratio, under inert atmosphere leads to the formation of $[\text{SnCl}_4(\text{N}=\text{CH}-\text{C}_6\text{H}_5)(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)]$, a SnCl_4 -imine complex, as colourless crystals. By using the same conditions, with $\text{Ph}_2\text{C}=\text{NMe}$ as Schiff's base, Clegg and colab. achieved *orto*-metallation, but in our case only complexation occurs.

The molecular structure of $[\text{SnCl}_4(\text{N}=\text{CH}-\text{C}_6\text{H}_5)(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)]$, determined by single crystal X-ray diffraction, comprises a coordination complex having a pentacoordinated tin atom, due to the strong $\text{N} \rightarrow \text{Sn}$ coordination of the *N*-(2,6-diisopropylphenyl)-1-phenylmethanimine ligand. The coordination geometry around the metal center is a slightly distorted trigonal bipyramid, with the

* Corresponding author: richy@chem.ubbcluj.ro; fax: (+40) 264-590818; tel: (+40) 264-593833

nitrogen atom from the (imino)aryl ligand in one of the axial positions (Fig. 1, Table 1). The tin atom is displaced from the Cl₃ equatorial plane towards the axial Cl by 0.12 Å. The Sn1-N1 bond length [2.312(4) Å] is somewhat longer than the one found in [SnCl₄{(N=CH-C₆H₅)(4-Cl)C₆H₃}₂] [2.267(2) Å]. The imine C7-N1 bond in [1.279(5) Å] is not affected by the coordination to SnCl₄ and is similar to other imine containing derivatives characterized. The (imino)aryl ligand adopts a *Z* configuration as a result of the coordination to the metal center, most probably to reduce steric repulsions between the organic fragments and the chlorine atoms. This configuration is also stabilized by an intramolecular C-H...π (Ph_{centroid}) contact (*i.e.* H...Ph_{centroid} contacts shorter than 3.1 Å, with an angle γ between the normal to the aromatic ring and the line defined by the H atom and Ph_{centroid} smaller than 30°)¹⁰ between one hydrogen atom of the benzyl fragment

and the aromatic ring bonded to N [C(6)-H(6)_{methylene}...Ph_{centroid}{C(8)-C(13)} 2.74 Å, $\gamma = 25.9^\circ$] (Fig. 2).

The axial Sn-Cl bond length is slightly longer than the equatorial ones [Sn1-Cl1 = 2.374(2) *vs.* Sn1-Cl2 = 2.304(2), Sn1-Cl3 = 2.323(2) and Sn1-Cl4 = 2.306(2) Å, respectively]. The distortion of the trigonal bipyramidal geometry on the axial positions is more pronounced compared to the coordination polyhedra found in [SnCl₄(C₇H₁₃N)],⁷ compound with shorter Sn-N and Sn-Cl [2.282(4) and 2.366(2) Å, respectively] axial bonds.

In crystal, the title compound forms dimers through hydrogen bonds interactions between Cl3 from one molecule and H20B from another molecule [Cl3...H20B' = 2.832 Å; symmetry equivalent position given by "prime": (2-x, 1-y, z); $\sum r_{vdw}(Cl,H)$ 3.01 Å¹¹] (Fig 2).

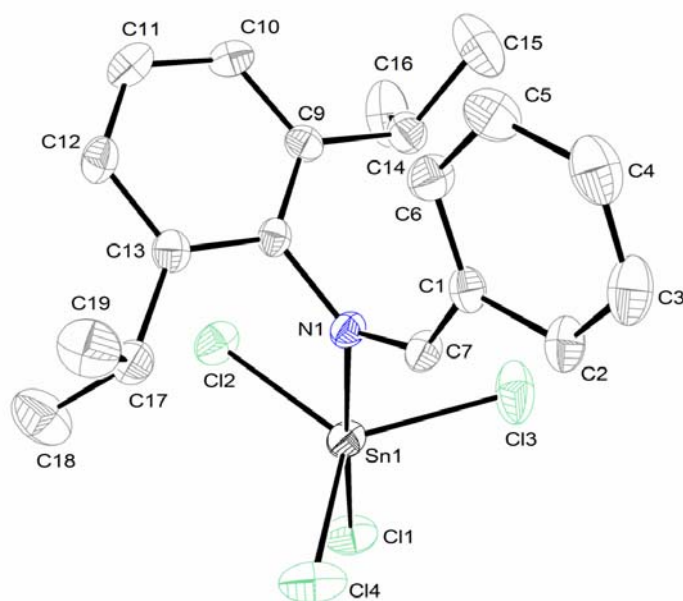


Fig. 1 – Molecular structure of [SnCl₄(N=CH-C₆H₅)(2,6-*i*-Pr₂)C₆H₃] showing 30% probability ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1

Selected interatomic distances (Å) and angles (°) in [SnCl ₄ (N=CH-C ₆ H ₅)(2,6- <i>i</i> -Pr ₂)C ₆ H ₃]			
Sn1-Cl1	2.374(2)	Sn1-Cl4	2.306(2)
Sn1-Cl2	2.304(2)	Sn1-N1	2.312(4)
Sn1-Cl3	2.323(2)		
N1-Sn1-Cl1	177.58(9)	N1-Sn1-Cl2	87.68(8)
Cl1-Sn1-Cl2	92.81(5)	N1-Sn1-Cl3	86.39(9)
Cl1-Sn1-Cl3	91.34(6)	N1-Sn1-Cl4	86.76(10)
Cl1-Sn1-Cl4	95.03(6)		
Cl2-Sn1-Cl3	122.17(7)	Cl3-Sn1-Cl4	116.85(7)
Cl2-Sn1-Cl4	120.14(6)		

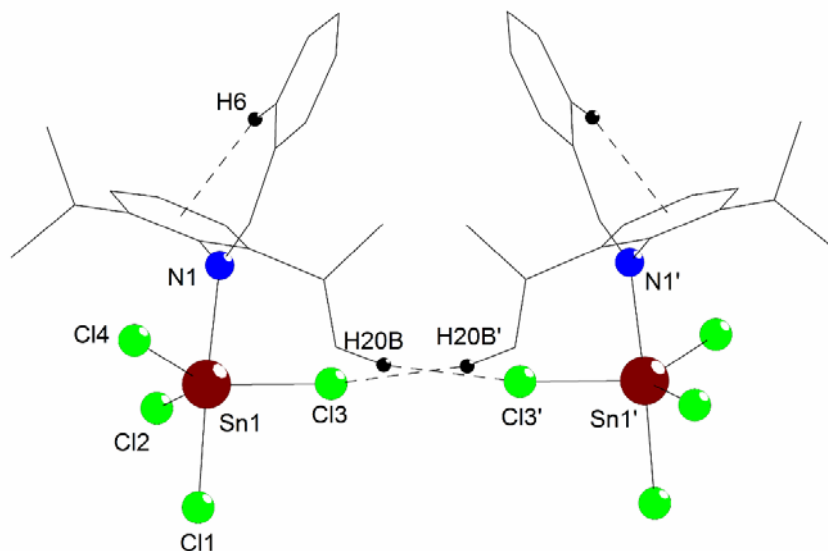


Fig. 2 – View of the dimer in the crystal of $[\text{SnCl}_4(\text{N}=\text{CH}-\text{C}_6\text{H}_5)(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]$ based on intermolecular $\text{Cl}\cdots\text{H}$ interactions [only hydrogens involved in interactions are shown; symmetry equivalent positions given by “prime”: $(2-x, 1-y, z)$].

Table 2

Crystal data and structure refinement of $[\text{SnCl}_4(\text{N}=\text{CH}-\text{C}_6\text{H}_5)(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]$	
Molecular formula	$\text{C}_{19}\text{H}_{23}\text{Cl}_5\text{Sn}$
<i>M</i>	525.87
Crystal system	Orthorhombic
Space group	<i>Aba</i> 2
Temperature (K)	297(2)
<i>a</i> /Å	19.947(13)
<i>b</i> /Å	16.504(11)
<i>c</i> /Å	13.414(9)
α /°	90
β /°	90
γ /°	90
<i>V</i> /Å ³	4416(5)
<i>Z</i>	8
<i>D</i> _{calc} /gcm ⁻³	1.582
<i>F</i> (000)	2096
μ (Mo-K α)/mm ⁻¹	1.644
Crystal size (mm ³)	0.29 x 0.28 x 0.24
θ range for data collection (°)	2.04 to 25.00
Reflections collected	20548
Independent reflections	3889 [R(int) = 0.0342]
Absorption correction	Multi-Scan ²⁵
Maximum and minimum transmissions	6937 and 0.6471
Data / restraints / parameters	3889 / 1 / 230
Goodness-of-fit on <i>F</i> ²	1.154
Absolute structure parameter	-0.02(2)
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ = 0.0319 <i>wR</i> ₂ = 0.0678
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0334 <i>wR</i> ₂ = 0.0685
Largest difference peak and hole (e Å ⁻³)	0.545 and -0.544

^a Definition of the *R* values: $R_1 = (\sum||F_o| - |F_c||) / \sum|F_o|$; $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

EXPERIMENTAL

The synthesis was carried out in argon atmosphere using Schlenk techniques. Toluene was dried and freshly distilled

prior to use. SnCl_4 was commercially available. $(\text{N}=\text{CH}-\text{C}_6\text{H}_5)(2,6\text{-iPr}_2\text{C}_6\text{H}_3)$ was prepared according to the literature method.¹²

Synthesis of [SnCl₄(N=CH-C₆H₅)(2,6-ⁱPr₂)C₆H₃]

SnCl₄ (0,22 g, 0.848 mmol) was added to a solution of (N=CH-C₆H₅)(2,6-ⁱPr₂)C₆H₃ (0,3 g, 1,13 mmol) (a 4:3 ratio) in toluene (10mL) and refluxed for 10 h. On cooling colourless crystals of the title compound formed. The compound is highly hydroscopic and as result only single crystal X-ray diffraction was performed.

Crystal structure determination

The intensity data of [SnCl₄(N=CH-C₆H₅)(2,6-ⁱPr₂)C₆H₃] were collected on a Bruker SMART APEX diffractometer with graphite-monochromated Mo-K α (0.7107 Å) radiation. Data were reduced and corrected for absorption. The software package SHELX-97 was used for structure solving and refinement.¹² Full-matrix least-squares refinements on F^2 were carried out using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Crystal and refinement data are listed in Table 2. Figures were created using ORTEP-III¹⁴ and Diamond 4¹⁵ software. Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 970737. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336033; e-mail:deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

CONCLUSIONS

A new coordination complex between SnCl₄ and the (N=CH-C₆H₅)(2,6-ⁱPr₂)C₆H₃ Schiff's base was obtained and characterized by single crystal X-ray diffraction. The tin atom in pentacoordinated with slightly distorted trigonal bipyramidal geometry. In solid state, the presence of Cl...H intermolecular interaction leads to the formation of dimer associations.

Acknowledgements: Financial support from National University Research Council (CNCSIS, Roumania; Research Project No. PN-II-RU-TE-2011-3-0033) is greatly appreciated. The support provided by the NATIONAL CENTER FOR X-RAY DIFFRACTION (Babes-Bolyai University, Cluj-Napoca, Roumania) for the solid state structure determinations is highly acknowledged.

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