

This work reports the synthesis and crystal structure characterization of new neutral hexacoordinated tin(IV) obtained by the reaction of SnX_4 $\text{X} = \text{Cl}, \text{Br}$ or I as starting materials with the O,N,N,O donor β -ketoiminate ligand (2Z,2'Z)-3,3'-(ethane-1,2-diylbis(azanediy))bis(1-phenylbut-2-en-1-one). The structural analysis of complexes **1-3** were carried out by single-crystal X-ray diffraction and solution ^{119}Sn NMR (except complex **3**) spectroscopies. The complexes showed distorted octahedral geometries with coordination skeleton at Tin atom of $\text{SnX}_2\text{N}_2\text{O}_2$.

Introduction and Objective

In continuation with our systematic investigations on hypercoordinated silicon and tin complexes [1]. The synthesis of these type of compounds which contain protic ligands, generally required the presence of base compounds as a proton extraction of the ligand, for example triethylamine [2]. The main objective of this work was to development a new methodology to obtain neutral hexacoordinated tin(IV) complexes without the use of triethylamine as base proton extraction. Herein we report the straightforward synthesis of neutral hexacoordinated tin(IV) complexes starting from SnX_4 $\text{X} = \text{Cl}, \text{Br}$ or I and symmetric β -ketoiminate ligand .

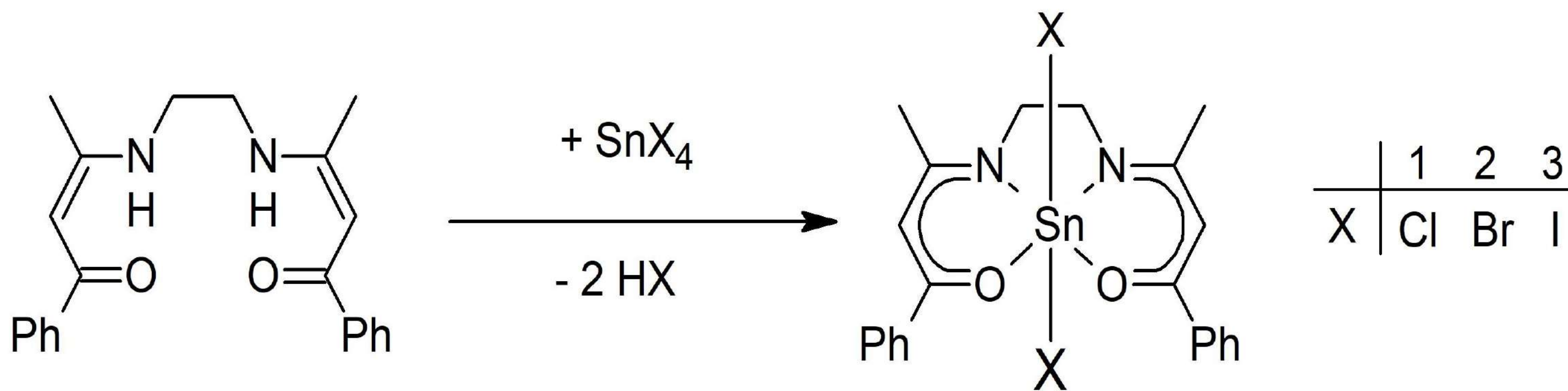
Experimental

The starting materials SnCl_4 and SnBr_4 were commercially available from Sigma Aldrich and SnI_4 was obtained as orange crystals with 60 % yield by the reaction of metallic tin with I_2 as show in the Scheme 1 [3].



Scheme 1

The new neutral hexacoordinated tin(IV) complexes **1-3** were obtained by the straightforward reaction of SnX_4 with I_2 with the β -ketoiminate ligand (Scheme 2) in dried acetonitrile.



Scheme 2

Suitable crystals for X-ray single-crystal diffraction were obtained by slow cooling a solution of complexes **1-3** from 60 ° to room temperature.

Equipment and Instruments



Schlenk Line



500 MHz NMR Spectrometer



Single-Crystal X-ray Diffractometer

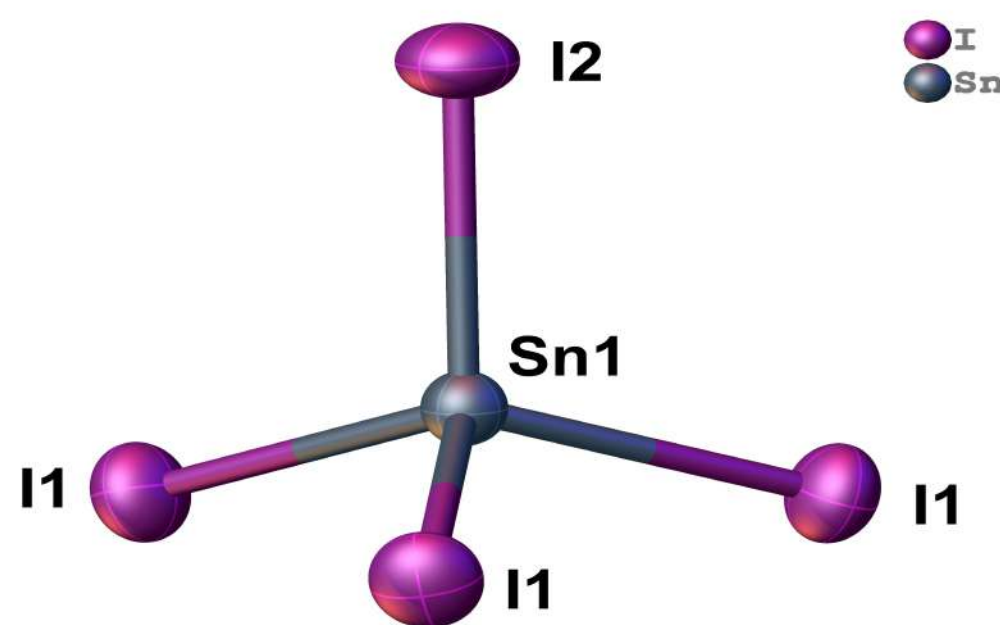
References

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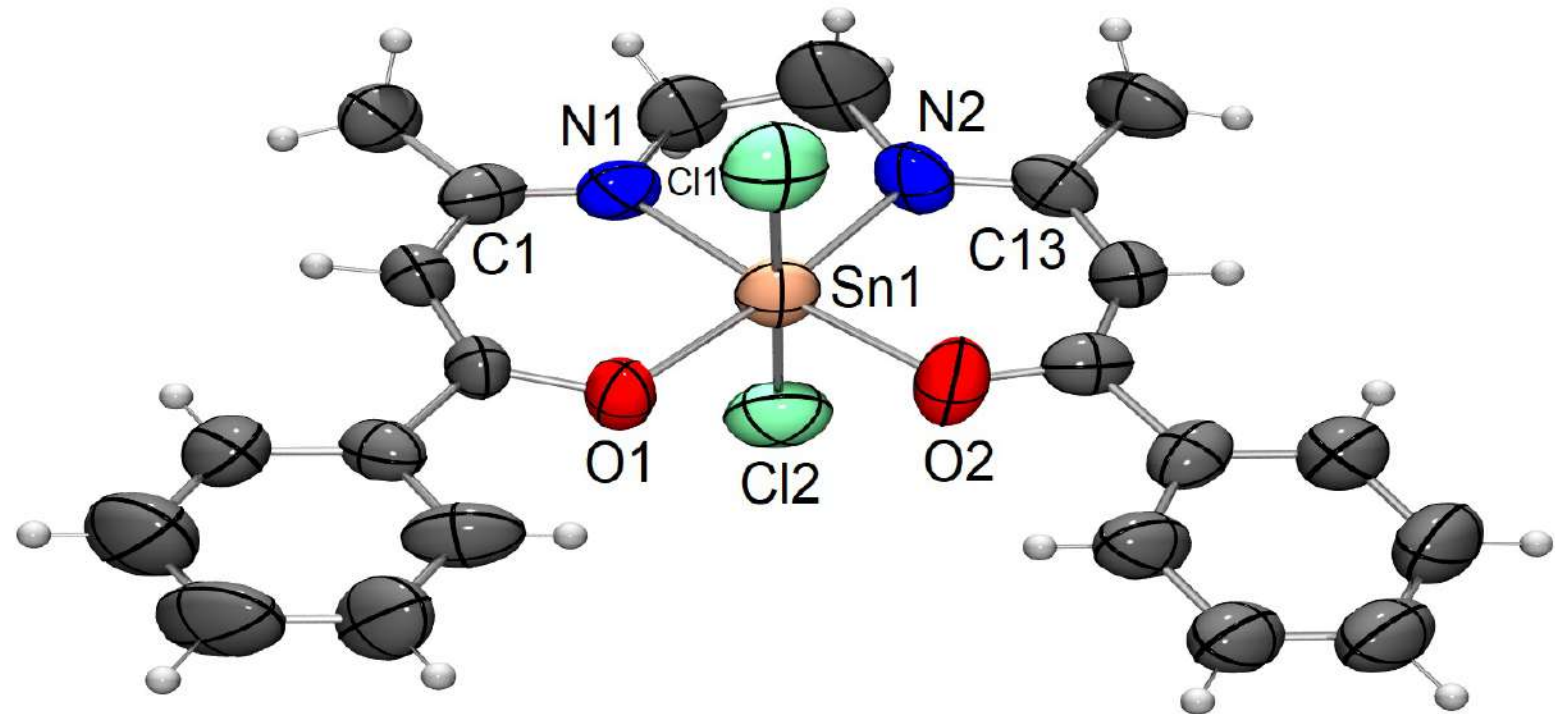
Acknowledgments



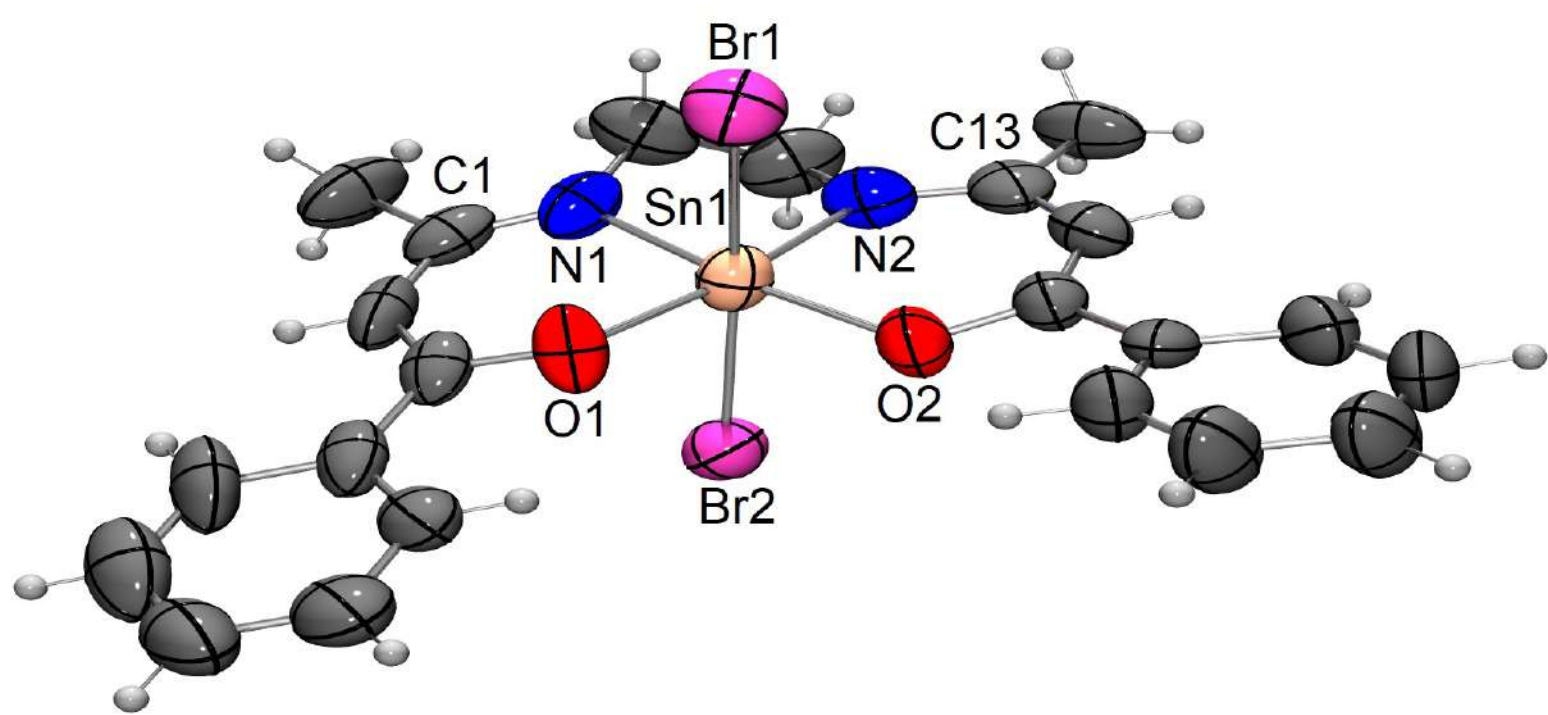
Results



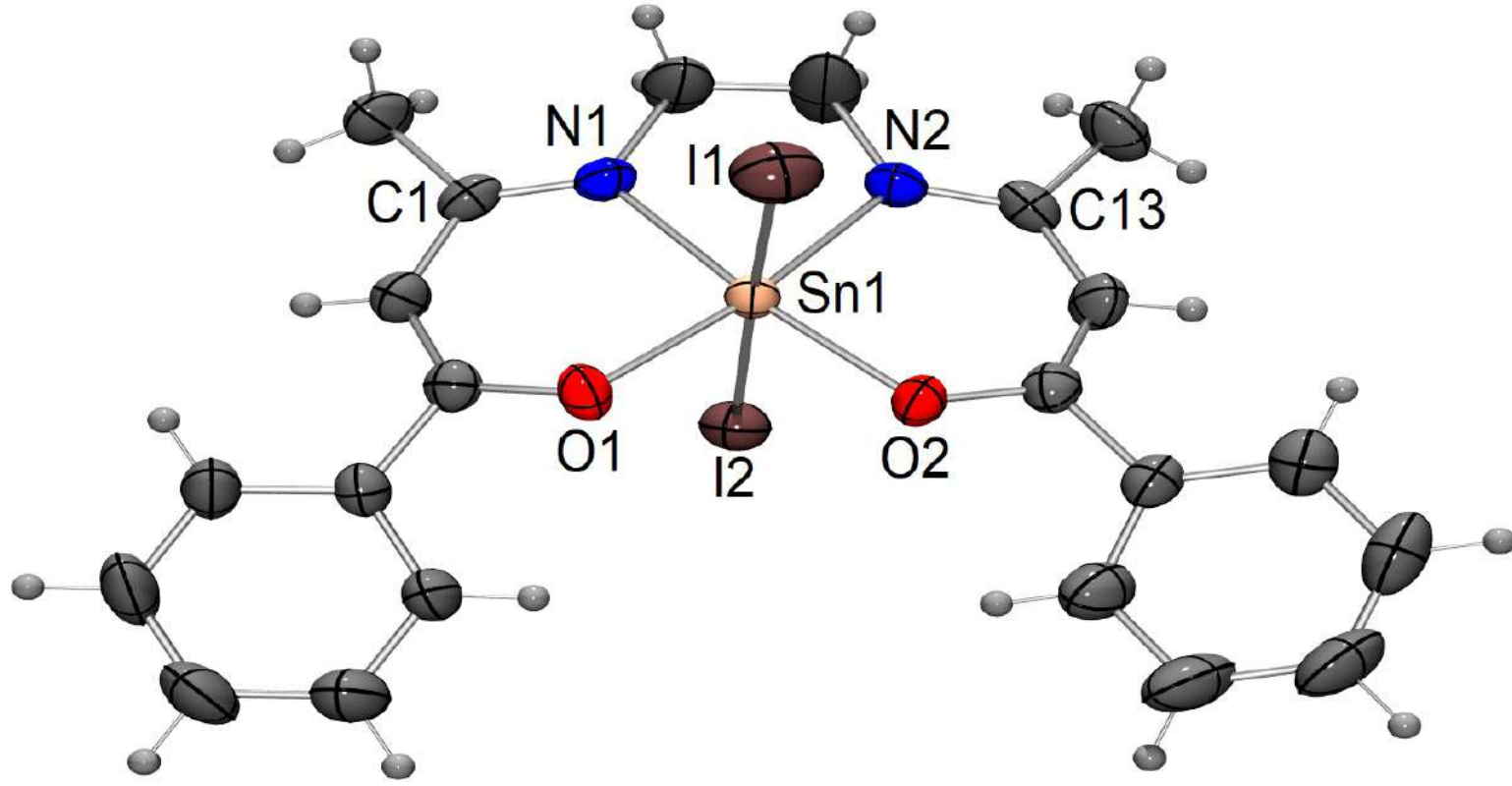
Ortep view of compound SnI_4



Ortep view of compound **1**



Ortep view of compound **2**



Ortep view of compound **3**

Crystal Data for I_4Sn ($M = 626.29$ g/mol): cubic, space group Pa-3 (no. 205), $a = 12.2847(6)$ Å, $V = 1853.93(16)$ Å³, $Z = 8$, $T = 293(2)$ K, $\mu(\text{MoK}\alpha) = 15.979$ mm⁻¹, $D_{\text{calc}} = 4.488$ g/cm³, 1682 reflections measured ($6.64^\circ \leq 2\theta \leq 58.12^\circ$), 699 unique ($R_{\text{int}} = 0.0504$, $R_{\text{sigma}} = 0.0726$) which were used in all calculations. The final R_1 was 0.0589 ($>2\sigma(I)$) and wR_2 was 0.1517

Crystal Data for $\text{C}_{24}\text{H}_{25}\text{Cl}_2\text{N}_3\text{O}_2\text{Sn}$ ($M = 577.06$ g/mol): monoclinic, space group P21/c (no. 14), $a = 15.5096(13)$ Å, $b = 14.2253(13)$ Å, $c = 11.6277(7)$ Å, $\beta = 95.212(7)^\circ$, $V = 2554.8(4)$ Å³, $Z = 4$, $T = 293(2)$ K, $\mu(\text{MoK}\alpha) = 1.234$ mm⁻¹, $D_{\text{calc}} = 1.500$ g/cm³, 11410 reflections measured ($6.72^\circ \leq 2\theta \leq 52.74^\circ$), 5044 unique ($R_{\text{int}} = 0.0485$, $R_{\text{sigma}} = 0.0672$) which were used in all calculations. The final R_1 was 0.0702 ($>2\sigma(I)$) and wR_2 was 0.2156.

Crystal Data for $\text{C}_{22}\text{H}_{22}\text{Br}_2\text{N}_2\text{O}_2\text{Sn}$ ($M = 624.95$ g/mol): monoclinic, space group P2₁/c (no. 14), $a = 15.6614(7)$ Å, $b = 14.2366(7)$ Å, $c = 11.6586(4)$ Å, $\theta = 94.423(4)^\circ$, $V = 2591.72(19)$ Å³, $Z = 4$, $T = 293(2)$ K, $\mu(\text{Mo K}\alpha) = 4.087$ mm⁻¹, $D_{\text{calc}} = 1.6015$ g/cm³, 8278 reflections measured ($6.7^\circ \leq 2\theta \leq 58.4^\circ$), 5365 unique ($R_{\text{int}} = 0.0207$, $R_{\text{sigma}} = 0.0441$) which were used in all calculations. The final R_1 was 0.0724 ($\geq 2\sigma(I)$) and wR_2 was 0.2480

Crystal Data for $\text{C}_{22}\text{H}_{22}\text{I}_2\text{N}_2\text{O}_2\text{Sn}$ ($M = 718.91$ g/mol): monoclinic, space group P2₁/c (no. 14), $a = 13.7901(6)$ Å, $b = 13.5275(5)$ Å, $c = 13.7655(6)$ Å, $\theta = 111.804(5)^\circ$, $V = 2384.19(17)$ Å³, $Z = 4$, $T = 293(2)$ K, $\mu(\text{MoK}\alpha) = 3.681$ mm⁻¹, $D_{\text{calc}} = 2.003$ g/cm³, 13013 reflections measured ($6.68^\circ \leq 2\theta \leq 52.74^\circ$), 4780 unique ($R_{\text{int}} = 0.0296$, $R_{\text{sigma}} = 0.0291$) which were used in all calculations. The final R_1 was 0.0340 ($>2\sigma(I)$) and wR_2 was 0.0904

Table 1. Selected bond lengths, ^{119}Sn NMR chemical shift and melting point.

Compound	Sn-X	Sn-O	Sn-N	^{119}Sn (δ)	Melting point °C
1	2.438 (3) 2.438 (3)	2.017 (6) 2.020 (6)	2.102 (6) 2.108 (7)	- 573.92	170 (dec.)
2	2.8358 (4) 2.7891 (4)	2.046 (3) 2.037 (3)	2.136 (3) 2.133 (3)	-1025.97	138 (dec.)
3	2.6053 (13) 2.5844 (14)	2.020 (6) 2.037 (7)	2.128 (8) 2.112 (8)	ND	140 (dec.)