Tin(IV) Complexes with Thiosemicarbazide and 4-Methyl-3-thiosemicarbazide Derivatives

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Dedicated to Professor Alfonso Castiñeiras on the Occasion of his 65th Birthday

Abstract. Five new complexes were isolated from a CH_2Cl_2 solution of $SnCl_4$ and the ligands benzil bis(thiosemicarbazone) L^1H_6 , benzil bis(4-methyl-3-thiosemicarbazone) $L^1Me_2H_4$, 5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]-triazine-3-thione, L^2H_2OMe and 5-methoxy-4-methyl-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]-triazine-3-thione, $L^2MeHOMe$. The characteristics of the complexes

analysis, mass spectrometry, IR, ¹³C and ¹¹⁹Sn CP/MAS NMR spectroscopy.

depend on the ligand. Compounds were characterized by elemental

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Introduction

During the last few decades there has been a growing interest in the pharmacological properties of thiosemicarbazones (TSCs) and their complexes, due to their ability to function as antiviral, antibacterial, antifungal and anticancer agents [1-4]. This activity is usually increased by complexation, therefore understanding of the properties of both ligand and metal can lead to the synthesis of highly active compounds. In this respect, tin compounds have interesting medical applications and understanding of the mechanism of their activity requires detailed knowledge of their structures and reactivities. In addition, the coordination chemistry of tin in solution and in the solid state is an attractive target for structural studies by means of spectroscopic and diffraction techniques. In particular, the great sensitivity of ¹¹⁹Sn NMR allows detecting subtle changes in the immediate surroundings of the tin atom [5].

Complexes of TSC ligands with non-transition metals such as tin have not received much attention, the majority are organotin(IV) compounds, and reports of non-organometallic tin complexes with thiosemicarbazones are scarce in the literature. Most of the complexes reported are with tridentate TSCs containing a pyridine ring, with the tin

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atom in an octahedral arrangement completed by halogen ligands [6, 7]. In addition, the generally poor solubility of group 14 metal complexes of anionic sulphur ligands makes it difficult to structurally characterize these systems and only few complexes have been studied by X-ray diffraction. The most common coordination numbers for tin(IV) are five or six. In fact, there are more than 3000 compounds with this coordination while only 39 are eight-coordinate. To date only three tin complexes with a N_4S_4 environment have been reported, [Sn(2-SC₅H₄N-3-SiMe₃)₄] [8], [Sn(3- $(CF_3-pyS)_4$ [9], both with bidentate pyridine-thione ligands and [Sn(ATSM)₂], with two tetradentate ligands, which has been recently published [10]. Due to the electronic delocalisation, which is enhanced upon deprotonation, TSC ligands are very versatile. This fact, together with the presence of different types of donor atoms, allows several coordination modes. So that, depending on the metal coordination preferences, a particular ligand can show different coordination behaviour. In particular, we have established in previous works that benzil bis(thiosemicarbazone), L¹H₆ acts, at least, as a N₂S₂ chelate, but depending on the metal preferences and/or the working conditions, the complexes show different grade of deprotonation in the ligand as well as a variety of structures. In fact, we have characterized complexes of this ligand acting as a neutral molecule with cadmium and mercury nitrate [11], as a monoanion in copper and zinc complexes [12] or as a dianionic ligand with different metals [11, 13]. $L^{1}H_{6}$ can act as tetradentate chelate giving mononuclear complexes [11-13], as chelate and bridge through a sulfur atom vielding a dinuclear structure and even as chelate and bridge via a nitrogen atom provided by one terminal amine in a coordination polymer [13]. The



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exception is the methyl mercury complex, in which only the sulfur atoms are bonded to two methyl mercury moieties in a binuclear structure [14].

On the other hand, triazine derivatives have traditionally found applications in analytical chemistry as complexation agents, in electrochemistry as multi-step redox systems and as pesticide or herbicide components in agriculture. In the last years, there has been a growing interest in these compounds that have been used, for example, as templates in multidimensional crystal engineering involving metal complexes for producing nanometre sized oligonuclear coordination compounds, as scaffold in combinatorial chemistry, as well as new building blocks in peptidomimetics and as anticancer agents [15, 16] Therefore, the synthesis of tin compounds with triazines derived from thiosemicarbazides is an interesting topic to pursue. We have characterized complexes of 5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]-triazine-3-thione, L²H₂OMe with divalent metal nitrates such as Co, Ni, Zn, Cd, Pb, as well as CuCl and some diorganic tin(IV) compounds. In all of them the ligand has lost a methanol molecule and an additional double CN bond has been formed, acting as a monoanion L^2 [17–19]. Those complexes are NS chelates, besides in Zn, Cd, Pb and Cu derivatives the S atom acts as a bridge, giving binuclear structures, except the copper(I) complex, which shows a hexanuclear structure. The triazine is only bonded through the sulfur atom in the mercury complexes giving a linear disposition for the mercury atom [20]. Here we report the syntheses and characterization of new complexes obtained by reaction of tin(IV) chloride with benzil bis(thiosemicarbazone) L^1H_6 , benzil bis(4-methyl-3-thiosemicarbazone) $L^1Me_2H_4$ and the triazine ligands 5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]-triazine-3-thione, L^2H_2OMe and 5-methoxy-4-methyl-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]triazine-3-thione, $L^2MeHOMe$.

Results and Discussion

Proposed structures for the ligands and their tin (IV) complexes are summarized in Schemes 1 and 2.

Formation of the tin(IV) complexes

All reactions were performed by mixing a suspension of the ligands in dichloromethane with a solution of tin(IV) chloride in the same solvent until a 1:1 or 1:2 mole ratio, with an scarce excess of metal salt was reached.

Analytical data of the complexes prepared from the open chain ligands, 1 and 2 indicate, respectively, a 2:1 and 1:1





molar ratio between the tin atom and the ligand as well as that the chloride ions remain in both compounds (Scheme 1). The FAB⁺ mass spectra of the complexes show a peak corresponding to the ligands and a peak corresponding to $[SnClL^1H_4]^+$ or $[SnClL^1Me_2H_2]^+$, respectively. The FAB⁻ spectrum of complex 1 suggests the presence of a halide tin(IV) ion complex. The experimental isotopic distribution for every peak fits the theoretical one.

The reactions with the cyclic ligands were carried out with two different Sn:Ligand molar ratio (1:1 and 1:2). Reactions of L^2H_2OMe , gave only complex 3, while the reactions with the 4-methyl-3-thiosemicarbazide derivative, $L^{2}MeHOMe$, allow to isolate two compounds, 4 and 5. The analytical data of complexes 3 and 4 show a 1:1 Sn:Ligand ratio, while a 1:2 ratio is observed for complex 5 (Scheme 2). Data for 3 indicate that the ligand has lost a methanol molecule, as it happened in all of its complexes previously characterized, which is consistent with the peak observed in the mass spectrum. Analysis for complex 4 indicate that one CH₃ group has been lost. The FAB⁺ mass spectra of 4 and 5 only show peaks corresponding to the interaction of the organic part of the complexes with the matrix used in the experiments (m-NBA). EI-MAS spectra of 4 and 5 show peaks corresponding to the organic part of the complexes, $[L^2H_2OMe]^+$ and $[L^2MeHOMe]^+$, respectively, confirming the loss of one methyl group in complex 4. The MALDI-MS spectrum of 5 confirms a 1:2 Sn : Ligand ratio.

All complexes are sensitive to the presence of moisture. In addition, the mother liqueurs from the reactions with $L^2MeHOMe$ change their colour in the presence of small amounts of moisture and a crystalline solid is separated. Its X-ray data confirms that the binuclear complex $[Sn_2Cl_6(OH)_2(H_2O)_2]$ ·3H₂O was formed. This compound was previously characterized by reaction of SnCl₄ and 3-acetyl-5-benzyl-1-phenyl-4,4-dihydro-1,2,4-triazine-6-one oxime in commercial CH₂Cl₂ [21].

Conductivity data of complexes in DMF indicate that the open chain derivatives are electrolytes, while the triazine complexes are molecular compounds [22].

Spectroscopic studies

The shifts observed in the IR spectra of complexes 1 and 2 with respect to the free ligands, indicate the coordination to the tin atom through the imine nitrogen and the sulfur atoms. In addition, both spectra show new bands corresponding to the new bonds formed and the band expected at low frequency corresponding to v(Sn-Cl) in $[SnCl_6]^{2-}$ was observed in complex 1.

Complexes 1 and 2 are sparingly soluble in the common deuterated solvents except donor ones. ¹H NMR spectrum of 2 in acetone indicates the loss of one of the acidic amine hydrogen, but in DMSO shows the partial decomposition of the complex, therefore, ¹³C and ¹¹⁹Sn NMR in the solid state were measured for both complexes. The ¹³C CP/MAS NMR spectra show the signal corresponding to the thioamide carbons shifted to high field and those corresponding to the imine carbon atoms shifted to low field. Therefore, both groups are bonded to the tin atom and the ligand acts as a chelate N₂S₂, as expected for both molecules. The different stoichiometry of complexes 1 and 2 is reflected in the number of carbon atoms in the ¹³C CP/MAS spectra. These differences can be explained by the presence in the complex 2 of two ligand molecules with an asymmetric behaviour and/or by the formation of a binuclear structure, as observed in the diphenyllead(IV) derivative [23].

The IR spectrum of 3 confirms the loss of the secondary amine hydrogen atom and the formation of an additional C=N bond. The shifts observed in the IR spectra of complexes 3 and 5, with respect to the free ligands, indicate the coordination to the tin atom through the sulfur atoms, besides some new bands can tentatively be assigned to Sn-Cl bonds. In the ¹H NMR spectrum of **3** the absence of any signal corresponding to the amine protons supports the presence of L^2 . In addition, the loss of the methoxy group is confirmed by the absence of the singlet corresponding to the OCH₃ moiety ($\delta = 3.4$). The ¹H NMR spectrum of 4 in DMF-d₆ shows signals indicating the partial decomposition of the complex, but in DMSO-d₆ two signals corresponding to amine hydrogen atoms, one corresponding to a methoxy group and the corresponding aromatic hydrogen are observed. These data suggest that the CH₃ bonded to the nitrogen atom has been substituted by one hydrogen atom.

In the ¹³C CP/MAS spectra of complexes derived from the cyclic ligands (3 and 5), the shifts observed in the thioamide carbon signals are indicative of coordination to the tin centre through the sulfur atom in both complexes. In the spectrum of complex 3, the absence of the carbon atom of the OCH₃ group and the additional signal in the range for a double CN bond confirm the above proposed modification. Therefore, in complex 3 the anionic ligand is bonded through the amine and the thioamide groups acting as a NS chelate as it was observed in the diorganotin complexes with this ligand with the same stoichiometry [19]. The spectrum of 5 also indicates that the imine group is not involved in the tin coordination. The coordination sphere on tin(IV) might be completed by three chloride ions in complex 3 and by four in complex 5 (Scheme 2). On the other hand, the ¹³C CP/MAS spectrum of complex 4, recorded in the same conditions of all the other compounds, shows signals at 172 ppm and 158 ppm, which correspond to a thiocarbonyl and a imine carbon atoms, one signal corresponding to the carbon atom of the OCH₃ group, and the absence of the quaternary and the methyl carbon atoms, which suggests that the ligand has suffered an important

change. The spectrum was also registered at 10 KHz and with a relaxation time of 20 s. The new spectrum shows an additional peak at 83.3 ppm assignable to a CNOR₂ carbon atom. The position of the signals suggests that the ligand is probably bonded by the imine nitrogen atom. The signals observed agree with the substitution of the methyl group bonded to the nitrogen atom by one hydrogen atom in the reaction medium. The surprising changes observed in L²Me-HOMe could be explained in base of an oxidative N-dealkylation of tertiary amines reaction, which can occur in CH₂Cl₂ and in the presence of a small excess of tin(IV) chloride, as it has been described in the literature under oxidative conditions [24].

It is well known that the ¹¹⁹Sn chemical shift is very sensitive to changes in the coordination number of the tin atom as well as to the nature of the bonding, so it is a useful tool to determine the environment of this metal in a complex in the absence of X-ray data. The signal of ¹¹⁹Sn spectra of complexes recorded in DMF (see experimental part) are found practically in the same positions (-631, -634 ppm), and they are very close to that observed for $SnCl_4(DMF)_2$ (-630 ppm), indicating that the solvent is coordinated to the metal atom displacing some atoms from the coordination sphere of the tin centre. The ¹¹⁹Sn CP/MAS spectra of complexes 1 and 2 show two signals, the MAS spectra obtained using a single pulse sequence with proton decoupling, suggest a 1:1 ratio for the signals in both complexes. The ¹¹⁹Sn chemical shifts observed in complex 1, -671 and -728 ppm, are indicative of Sn(IV) in a hexacoordinate environment, the more negative value is consistent with the presence of the $[SnCl_6]^{2-}$ ion [25-28]. The lower value is in the high range for this coordination number with a N₂S₂Cl₂ coordination, where the presence of chloride ions leads to a more negative value of the chemical shift, due to its inductive effect and also the possibility of additional π -contribution to the Sn-Cl bond, which would shield the nucleus to a greater extent [29]. The signals observed in complex 2, -659 and -718 ppm, fall between the ranges of hexacoordinate or heptacoordinate tin(IV) complexes. In accordance with the composition of this complex, the presence of two tin(IV) atoms means the presence of two ligands. Taking into account the number and position of the ¹³C signals and the values of the ¹¹⁹Sn NMR spectra, complex 2 might contain two Sn(IV) ions joined by sulfur bridges in a binuclear structure, in a similar disposition than $L^1H_4^{2-}$ in the cadmium complex [13] and as $L^1Me_2H_2^{2-}$ in the diphenyllead(IV) derivative [23]. In complex 2, one of the ligands acts as a dianion and the other one would be in the neutral form. Therefore, one of the tin atoms would have an octahedral coordination, S_3Cl_3 and the other $S_3N_2Cl_2$ corresponding to the signals at -659 and -718 ppm respectively (Scheme 1).

The ¹¹⁹Sn CP/MAS spectra of complexes 4 and 5 show one signal at -612 and -672 ppm, respectively. It was not possible to get a useful spectrum of complex 3. The presence of one signal agrees with a monomer structure or a centrosymmetric dimeric structure for both complexes. The values are in agreement with a NCl₄ coordination in complex **4** and with an octahedral coordination on the tin(IV) atom with a S_2Cl_4 coordination sphere in complex **5**.

Experimental Section

Physical Methods

IR spectra in the 4000-400 cm⁻¹ range were recorded as KBr pellets on a Jasco FT/IR-410 spectrophotometer, and in the $560{-}20\,cm^{-1}$ range on a FT-IR Bruker IFS60v one. 1H and ^{13}C NMR spectra were recorded on a spectrometer Bruker AMX-300 using DMSO-d₆, CDCl₃, acetone-d₆, methanol-d₄ or DMF-d₆ as solvents and TMS as internal reference. 119Sn NMR spectra were recorded in the same spectrometer using DMF-d₆ or DMF+CDCl₃ as solvents and using absolutes references [30]. Solid state NMR spectra were recorded at 298 K in a Bruker AV400WB spectrometer equipped with a 4 mm MAS-NMR probe (magicangle spinning). ¹³C CP/MAS NMR was obtained usingcross-polarization pulse sequence. The external magnetic field was 9.4 T and the sample was spun at 10 - 14 KHz, spectrometer frequencies were set to 100.61 MHz. For the recorded spectra a contact time of 4 ms were used and recycle delays of 4 s were used. Spectrum of complex 4 also was registered at 10 KHz with a relaxation time of 20 s. Chemical shifts are reported relative to TMS, using the CH group of adamantano as a secondary reference (29.5 ppm) [31]. ¹¹⁹Sn MAS NMR spectra were recorded at 149.1 MHz, on a Bruker AV 400 WB spectrometer equipped with a 4 mm MAS-NMR probe (magic-angle spinning). Spectra were taken on samples spinning at a rate of 5, 10 and 12 kHz in two ways: using a single pulse sequence of 3 µs ¹¹⁹Sn 40° with TPPM proton decoupling followed by a relaxation delay of 40-60 s and with CP sequence. The ¹¹⁹Sn-¹H Hartmann-Hahn conditions were optimised with tetraphenyltin. The CP-MAS spectra were obtained using spinning rates of 10 KHz, pulse delays of 30 s, contact times of 8 ms and TPPM high power proton decoupling. Chemical shifts are reported relative to tetramethyltin, using tin(IV) oxide as a secondary reference (-604.3 ppm) [32].

EI and fast atom bombardment (FAB) mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzylalcohol (*m*NBA) as the matrix in the FAB experiment. Conductivity data were measured using freshly prepared DMF solutions (ca. 10^{-3} M) at 25 °C with a Metrohm Herisau model E-518 instrument.

Spectroscopic data of organic molecules

Benzil bis(thiosemicarbazone), $L^{1}H_{6}$ [11]: Selected spectroscopic data: FAB⁺ (m/z): 357 ([M + 1]⁺, 100 %), 714 ([2M + 1]⁺, 25 %). ¹H NMR (DMSO-d₆, 300 MHz, 25 °C): δ = 9.8 (2H, NH, s); δ = 8.6 (2H, NH, s); δ = 8.3 (2H, NH, s); δ = 7.7 (4H, Ph, m); δ = 7.4 (6H, Ph, m). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ = 8.8 (2H, NH, s); δ = 7.6 (6H, Ph, m); δ = 7.4 (9H, Ph, m); δ = 6.6 (2H, NH, s); δ = 7.6 (6H, Ph, m); δ = 7.4 (9H, Ph, m); δ = 6.6 (2H, NH, s); δ = 140.5 (CN); δ = 133.1, 130.1, 128.9, 126.8 (Ph). ¹³C CP/MAS NMR (300 MHz, 25 °C): δ = 181.1 (CS); δ = 142.9 (CN); δ = 133.3, 132.4 130.1 (Ph). IR (KBr): v(N-H) 3420, 3386, 3342, 3330, 3210, 3151 s, v(C=N) 1608 w, δ (NH₂) 1581 s and v(CS) 848 w cm⁻¹.

Benzil bis(4-methyl-3-thiosemicarbazone), $L^{1}Me_{2}H_{4}$ [33]: Selected spectroscopic data: FAB^{+} (m/z) 385.2 ([M+1]⁺, 80 %), 769.6 ([2M+1]⁺, 10 %). ¹H NMR (DMSO-d₆, 300 MHz, 25 °C): $\delta = 9.8$ (2H, NH, s); $\delta = 8.9$ (2H, NH, q); $\delta = 7.7$ (4H, Ph, m); $\delta = 7.4$ (6H, Ph, m); $\delta = 3.0$ (6H, CH₃, d). ¹H NMR (CDCl₃, 300 MHz, 25 °C): $\delta = 8.5$ (2H, NH, s); $\delta = 7.8$ (2H, NH, q); $\delta = 7.7$ (4H, Ph, m); $\delta = 7.3$ (6H, Ph, m); $\delta = 3.3$ (6H, CH₃, d). ¹³C NMR (DMSO-d₆, 300 MHz, 25 °C): $\delta = 178.6$ (CS); $\delta = 140.4$ (CN); $\delta = 133.2$,

130.3, 129.1, 126.8 (Ph); δ = 31.5 (CH₃); ¹³C CP/MAS NMR (300 MHz, 25 °C): δ = 177.2 (CS); δ = 139.8 (CN); δ = 130.6–124.7 (Ph); δ = 32.1 (CH₃). **IR** (KBr): v(NH) 3435 and 3335 s, v(C=N) 1601 w, δ (HNC) 1546 s, v(CS) 845 w cm⁻¹.

5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]triazine-3-thione, $L^{2}H_{2}OMe$ [34, 35] Selected spectroscopic data: FAB⁺ (m/z): 266.2 ([M-OCH₃]⁺, 10 %), 298.2 ([M+1]⁺, 35 %). ¹H NMR (CDCl₃, 300 MHz 25 °C): δ = 9.5 (1H, NH, s); δ = 7.6 (2H, Ph, m); δ = 7.4 (2H, Ph, m); δ = 7.3–7.1 (6H, Ph, m); δ = 6.9 (1H, NH, s); δ = 3.4 (3H, OCH₃, s). ¹³C NMR (CDCl₃, 300 MHz, 25 °C): δ = 169.7 (CS); δ = 142.4 (CN); δ = 141.7, 133.7, 129.8, 126.5 (Ph); δ = 83.2 (CNOR₂); δ = 50.7 (CH₃O). ¹³C CP/MAS NMR (300 MHz, 25 °C): δ = 168.4 (CS); δ = 146.0 143.4 (CN); δ = 132.4, 131.3, 129.8. 127.0 (Ph); δ = 85.4 (CNOR₂); δ = 53.4 (CH₃O). IR (KBP): v(NH) 3184 s and 3131 s, v(C=N) 1608 w, δ (NCS) 1550 s, v(CS) 846 w cm⁻¹.

5-methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]triazine-3-thione, L²MeHOMe [33]: Selected spectroscopic data: **FAB**⁺ (m/z): 77.0 ($[C_6H_5]^+$, 9%), 105.1 ($[C_7H_6N+1]^+$, 20%), 118.1 ($[C_7H_6N_2]^+$, 8%), 280.2 ($[C_1_6H_1_4N_3S]^+$, 13%), 312.2 ($[M+1]^+$, 100%), 622.5 ($[2M+1]^+$, 10%). ¹H NMR (DMSO-d_6, 300 MHz, 25 °C): \delta = 12.3 (1H, NH, s); \delta = 7.5-7.2 (10H, Ph, m); \delta = 3.2 (3H, OCH₃, s); \delta = 2.9 (3H, CH₃, s). ¹H NMR (CDCl₃, 300 MHz, 25 °C): \delta = 9.5 (1H, NH, s); \delta = 7.6-7.1 (10H, Ph, m); \delta = 3.4 (3H, OCH₃, s); \delta = 3.1 (3H, CH₃, s). ¹³C NMR (DMSO-d_6, 300 MHz 25 °C): \delta = 171.7 (CS); \delta = 141.4 (CN), \delta = 139.9, 133.7, 129.3, 128.8, 127.9, 126.8, 126.4 (Ph); \delta = 87.1 (CNOR₂); \delta = 51.1 (OCH₃); \delta = 33.3 (CH₃). ¹³C CP/MAS NMR (300 MHz, 25 °C): \delta = 173.1 (CS); \delta = 146.1 (CN); \delta = 140.4, 135.1, 129.4, 128.6, 126.6 (Ph); \delta = 87.8 (CNOR₂); \delta = 52.1 (NCH₃); \delta = 37.1 (NCH₃). **IR** (KBr): v(NH) 3229 s, v(CN) 1589 w, δ (NCS) 1511 s, v(CS) 845 w cm⁻¹.

Synthesis of complexes

All the reactions were carried out under Ar atmosphere and the dichloromethane (DCM) was dried by refluxing over CaH₂.

[SnL¹H₆Cl₂][SnCl₆] (1): Over a suspension of L¹H₆ (0.20 g, 0.56 mmol) in 50 mL of dichloromethane were added dropwise and in the presence of argon 4 mL (0.69 mmol) of SnCl₄ solution in DCM (1 mL /49 mL). This solution was used for the synthesis of all of the coordination compounds. The mixture was stirred at room temperature for 12 h. The yellow solid formed was filtered off under argon atmosphere, washed with DCM and dried in vacuo. Yield 95 %. Mp 220 °C. $\Lambda_{\rm M}$ (DMF, Ω^{-1} cm²ml⁻¹): 103. Anal. Calc. for C₁₆H₁₆N₆S₂Cl₈Sn₂: C, 22.83; H, 1.80; N, 9.98; S, 7.60; Found: C, 23.28; H, 2.08; N, 10.16; S, 7.61 %.

FAB⁺ (m/z): 357.0 ([L¹H₆+1]⁺, 25 %), 508.8 ([SnClL¹H₄]⁺, 100 %). **FAB**⁻ (m/z): 296.8 ([SnCl₅]⁻, 48 %). ¹³**C CP/MAS NMR** (300 MHz, 25 °C): δ = 174.2 (CS); δ = 156.0 (CN); δ = 136.0, 133.3, 130.9, 128.0, 126.2 (Ph). **IR** (KBr): v(NH) 3459, 3347, 3270, 3186 s, v(C=N) 1612 w, δ(NH₂) 1541 s, δ(NCS) 1416 s, v(CS) 809 w, v(SnCl) 303 w, cm⁻¹. ¹¹⁹**Sn CP/MAS NMR** (300 MHz, 25 °C): δ = -670.9, -728.3.

[Sn₂L¹Me₂H₄L¹Me₂H₂Cl₅]Cl.CH₂Cl₂ (2): 4 mL (0.69 mmol) of the SnCl₄ solution were added over a solution of L¹Me₂H₄ (0.22 g, 0.56 mmol) in 50 mL of DCM. The mixture was stirred for 6 h and the pale orange solid formed was filtered off washed with DCM and dried in vacuo. Yield 80 %. Mp 227 °C. $\Lambda_{\rm M}$ (DMF, Ω^{-1} cm²ml⁻¹): 60. Anal. Calc. for C₃₇H₄₀N₁₂S₆Cl₈Sn₂: C, 34.11; H, 3.07; N, 12.90; S, 9.83; Sn, 18.28; Found: C, 33.92; H, 3.10; N, 12.64; S, 9.51; Sn, 18.87 %.

 $\begin{array}{l} \textbf{FAB}^{+} \ (\text{m/z}): \ 385.1 \ ([L^2Me_2H_4+1]^+, \ 15 \ \%), \ 537.0 \ ([SnClL^2Me_2H_2]^+, \ 30 \ \%) \\ \text{and} \ 572 \ ([SnCl_2L^2Me_2H_3]^+, \ 5 \ \%). \ ^{1}\textbf{H} \ \textbf{NMR} \ (\text{acetone-}d_6, \ 300 \ MHz, \\ 25 \ ^{\circ}\text{C}): \delta = \ 9.2 \ (\text{s}, \ 1.5 \ \text{H}, \ \text{NH}); \ \delta = \ 8.7 \ (\text{s}, \ 1.5 \ \text{H}, \ \text{NH}); \ \delta = \ 7.8 \ (\text{m}, \ 4H, \ \text{Ph}); \\ \delta = \ 7.4 \ (\text{m}, \ 10H, \ \text{Ph}); \ \delta = \ 5.6 \ (\text{s}, \ 2H, \ \text{CH}_2\text{Cl}_2); \ \delta = \ 3.2 \ (\text{d}, \ 6H, \ \text{CH}_3). \ ^{13}\text{C} \\ \textbf{CP/MAS} \ \textbf{NMR} \ (300 \ \text{MHz}, \ 25 \ ^{\circ}\text{C}): \ \delta = \ 175.1, \ 171.8, \ 169.6 \ (\text{CS}); \ \delta = \ 152.8, \\ 148.6 \ (\text{CN}); \ \delta = \ 134.7, \ 133.2, \ 131.2, \ 129.9, \ 128.2 \ (\text{Ph}); \ \delta = \ 33.8 \ (\text{CH}_3). \ \text{IR} \\ (\text{KBr}): \ v(\text{NH}) \ \ 3302 \ \text{s}, \ 3167 \ \text{s}, \ v(\text{C=N}) \ \ 1696 \ \text{w}, \ \delta(\text{HCN}) \ 1585 \ \text{s}, \ 1579 \ \text{s}, \\ \delta(\text{NCS}) \ 1599 \ \text{s}, \ v(\text{CS}) \ 906 \ \text{w}, \ 847 \ \text{w}, \ v(\text{SnCl}), \ v(\text{SnL}) \ \text{several bands} \ 320-280 \ \text{s} \\ \textbf{m}^{-1}. \ \ ^{19}\text{Sn} \ \textbf{NMR} \ (\text{DMF} \ + \ \text{CDCl}_3, \ 25 \ ^{\circ}\text{C}): \ \delta = \ -634.5 \ \text{ppm}. \ ^{119}\text{Sn} \ \textbf{CP/} \\ \textbf{MAS} \ \textbf{NMR} \ (300 \ \text{MHz}, \ 25 \ ^{\circ}\text{C}): \ \delta = \ -658.7 \ \text{and} \ -718.2. \end{array}$

[SnL²Cl₃].CH₂Cl₂ (3): 5 mL (0.87 mmol) of the SnCl₄ solution were added over L²H₂OMe (0.20 g, 0.67 mmol). Immediately, a golden

yellow solution was formed and then was stirred for 24 h at room temperature. An orange solid was formed by slow evaporation of the solvent. The solid was filtered and dried in vacuo. Yield 76 %. M.p. 178 °C. $\Lambda_{\rm M}$ (DMF, Ω^{-1} cm²ml⁻¹): 30. Anal. Calc. for C₁₆H₁₂N₃SCl₅Sn: C, 34.24; H, 2.14; N, 7.50; S, 5.71; Found: C, 33.95; H, 2.17; N, 7.70; S, 5.46 %.

FAB⁺ (m/z): 266.0 ($[L^2+1]^+$, 95 %), 419.0 ($[SnL^2HC1 + 1]^+$, 5 %), 453.8 ($[SnL^2Cl_2]^+$, 4 %), 489.7 ($[M+1]^+$, 7 %). ¹H NMR (acetone- d₆, 300 MHz, 25 °C): $\delta = 7.7$ -7.4 (Ph); $\delta = 5.6$ (s, 2H, CH₂Cl₂). ¹³C NMR (methanol-d₄, 300 MHz, 25 °C): $\delta = 170.0$ (CS); $\delta = 150.0$, 143.1 (CN); $\delta = 130.3$, 129.6, 127.8 (Ph). ¹³C CP/MAS NMR (300 MHz, 25 °C): $\delta = 171.0$ (CS); $\delta = 164.1$, 152.6 (CN); $\delta = 139.0$, 130.3, 129.6, 129.3, 129.0, 127.8 (Ph). **IR** (KBr): v(C=N) 1596, 1580 w, v(CNS) 1493, v(CS) 800 cm⁻¹.

The same compound was obtained when the reaction was carried out with a 1:2 tin : ligand ratio

[SnL²H₂OMeCl₄] (4): 5 mL (0.87 mmol) of the SnCl₄ solution were added over L²MeHOMe (0.21 g, 0.67 mmol). Immediately, an intense orange solution was formed, which was stirred for 6 h at room temperature. A microcrystalline orange solid was formed overnight and it was separated by filtration. Yield 72 %. M.p. 235 °C. Λ_M (DMF, Ω^{-1} cm²ml⁻¹): 14. Anal. Calc. for C₁₆H₁₅N₃SOCl₄Sn: C, 34.42; H, 2.67; N, 7.53; S, 5.76; Sn, 21.27; Found: C, 35.27; H, 2.67; N, 7.66; S, 5.85; Sn, 21.55 %.

EI-MS (m/z): 297.0 ([L²H₂OMe]⁺, 60 %). ¹H NMR (DMF-d₆, 300 MHz, 25 °C): $\delta = 12.0$ (1.5 H, NH, s); $\delta = 8.1$ (1 H, NH, s); $\delta = 7.7$ -7.1 (24 H, Ph, m); $\delta = 3.8$ (4H, CH₃, s); $\delta = 3.1$ (3H, CH₃, s). ¹H NMR (DMSO-d₆, 300 MHz, 25 °C): $\delta = 11.9$ (1H, NH, s); $\delta = 8.2$ (1 H, NH, s); $\delta = 7.6$ -7.1 (10 H, Ph, m); $\delta = 2.9$ (3H, CH₃, s). ¹³C CP/MAS NMR (300 MHz, 25 °C): $\delta = 171.8$ (CS); $\delta = 158.0$ (CN); $\delta = 133.6$, 131.5, 129.5, 127.4, 125.9 (Ph); $\delta = 49.1$ (OCH₃). ¹³C CP/MAS NMR (t = 20 s): $\delta = 171.8$ (CS); $\delta = 158.0$ (CN); $\delta = 133.7$, 131.5, 129.6, 128.8, 127.4, 125.9 (Ph); $\delta = 83.3$; $\delta = 49.1$ (OCH₃). II (KBr): v(C=N) 1597 w, v(CNS) 1497 s, v(CS) 847 w, v(SnCI) 312 w cm⁻¹. ¹¹⁹Sn NMR (DMF-d₆, 300 MHz, 25 °C): $\delta = -633.0$. ¹¹⁹Sn CP/MAS NMR (300 MHz, 25 °C): $\delta = -612.1$.

[Sn(L²MeHOMe)₂Cl₄] (5): 2 mL (0.33 mmol) of the SnCl₄ solution were added over L²MeHOMe (0.22 g, 0.67 mmol). Immediately, an orange solution was formed that was stirred for 6 h at room temperature. A yellow solid was formed by slow evaporation of the solvent; it was filtered off and dried in vacuo. Yield 64 %. M.p. 191 °C. $\Lambda_{\rm M}$ (DMF, Ω^{-1} cm²ml⁻¹): 16. Anal. Calc. for C₃₄H₃₄N₆S₂Cl₄Sn: C, 46.20; H, 3.80; N, 9.51; S, 7.24; Sn, 13.40; Found: C, 45.48; H, 3.75; N, 9.42; S, 7.34; Sn, 13.50 %.

EI-MS (m/z): 280.0 ([L²MeH]⁺, 20 %), 311.0 ([L²MeHOMe]⁺, 63 %). **MALDI-MS** (m/z): 430.0 ([Sn(L²MeOMe)]⁺, 20 %), 774.9 ([Sn(L²MeOMe)₂Cl]⁺, 15 %). ¹³C **CP/MAS NMR** (300 MHz, 25 °C): $\delta = 163.1$ (CS); $\delta = 145.6$ (CN); $\delta = 139.0$, 132.9, 130.6, 129.2, 128.2, 126.2 (Ph); $\delta = 89.2$ (CNOR₂); $\delta = 52.4$ (OCH₃); $\delta = 36.9$ (NCH₃). **IR** (KBr): v(C=N) 1610, 1594 w, v(CNS) 1490 s, v(CS) 843 w, v(SnCl) 312 w, v(SnCl) 298 w cm⁻¹. ¹¹⁹Sn NMR (DMF+CDCl₃, 300 MHz, 25 °C): $\delta = -634.3$. ¹¹⁹Sn CP/MAS NMR (300 MHz, 25 °C): $\delta = -672.1$.

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