INORGANIC ELECTROSYNTHESIS: A GREEN CHEMICAL METHOD FOR TIN COMPLEXES

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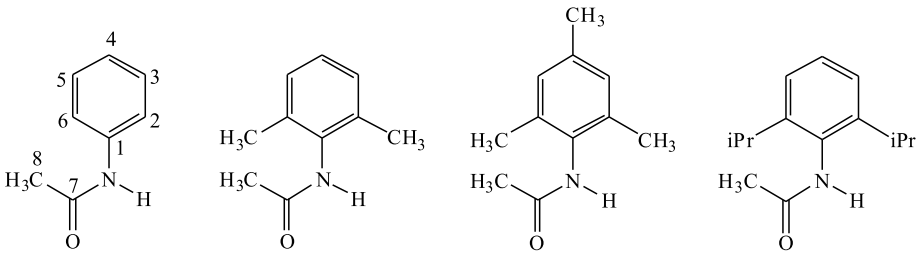
Abstract

Sn^{IV} complexes of the series of bulky amines have been reported by electrochemical oxidation (3 h) of a tin anode in a cell containing methanol solution of the corresponding bulky amine. All were full characterized by ^{1}H and ^{13}C-NMR, IR, and high resolution mass spectrometry. However, all were not enough soluble in organic solvent in order to record its ^{119}Sn-NMR spectra, this unusual behavior was attributed to the polymeric association thought intermolecular coordination OSn.

1. Introduction

Nowadays, it is well-know that there are several chemical synthetic pathways. However, inorganic electrosynthesis has become recognized as one of the most important synthetic pathways due to reduction of waste, reduction of energy consumption, scalable to industrial level, and environment-friendly method. Therefore, the electrosynthesis is a promising "*green method"* in chemistry [1]. Nevertheless, the electrochemical synthesis of coordination compounds of main group elements has been scarcely studied [2]. This method has advantages over the chemical synthesis *e.g.* short reaction times, reactions at room temperature, good yields and cheaper method. Actually, there are few reports on the literature about electrosynthesis of organotin complexes [3].

Tin complexes have been widely studied in the last four decades due to their important contribution in medicine [4], chemistry of materials [5], industrial application [6], and catalysis [7]. Tin compounds are potentially active as anticancer agent *e. g.* adducts with dative bonds such as NSn and OSn were found to be effective against lymphocytic leukemia P388 cells in rats [8] and breast (MCF-7, EVSAT), colonic (WiDr), ovarian (IGROV) and renal (A498) carcinoma and melanoma (M19 MEL) cell lines [9], respectively. It has been reported the adducts of organotin compounds with imidodiphosphinate ligands are promising anticancer agents against *Staphylococcus aureus [10]*. We have been involved in the synthesis and characterization of penta- and hexacoordinated organotin compounds derived from ligand with donor atoms [11,12]. Continuing with our research on this subject in this article, we will describe the electrosynthesis of a short series of tin compounds derived from bulky amines **1-4** (scheme 1).



1 **2** **3** **4**

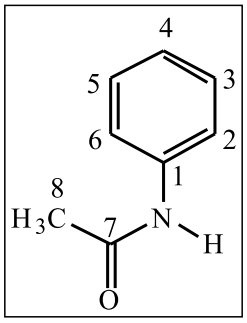
Scheme 1. Bulky amines **1-4**.

2. Experimental Section

Acetic anhydride, anilines (Aldrich) and all other reagents were used without further purification. Tin (Aldrich) was used in a rod form and was cleaned in dilute hydrochloric acid prior to electrolysis. High-resolution mass spectra were obtained by LC/MSD TOF on an Agilent Technologies instrument with APCI as ionization source. IR spectra were obtained with FT-IR 1600 Perkin Elmer. The $CDCl_3$ solvent used for NMR measurements was used without further purification. Melting points were obtained on a Mel-Temp II apparatus. NMR spectra were recorded by using JEOL GSX 270: ^{1}H (270.16 MHz) and ^{13}C (67.9 MHz).

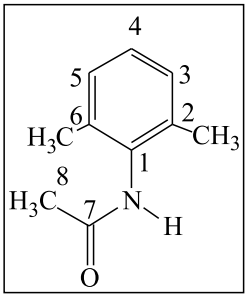
2.1 Synthesis of ligands

Synthesis of acetanilide 1 [13].



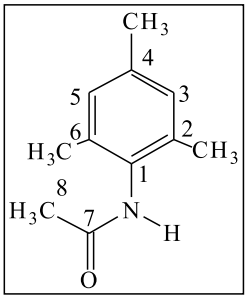
To solution of aniline (1 g, 10.73 mmol) in acetic anhydride (5 mL, in excess) was added water (20 mL). A precipitate was formed immediately. After 2h the solution was filtrated and washed with solution of NaOH (2 %) and then cold water to afford a white solid (1.3 g, 91 %). M. p: 113-115 °C (lit m. p. 113-115 °C). ^{1}H NMR (270.16 MHz, $CDCl_3$): 2.12 (s, CH_3, H-8, 3H), 7.07 [t, H-2, ^{3}J = 7.2 Hz, 1H], 7.26 [t, H-3, H-5, ^{3}J = 7.2 Hz, 2H], 7.49 [t, H-3, ^{3}J = 7.2 Hz, 2H], 8.17 (bs, -NH, 1H). ^{13}C NMR (67.93 MHz, $CDCl_3$): 24.3 (C8), 120.09 (C2, C6), 124.2 (C4), 128.8 (C3, C5), 168.9 (C7). HRMS; (TOF) *m/z :* [M^+] 136.08, (error 1.8275). IR (ATR) cm^{-1}: 3290.16 (m, NH), 2995.02 (m, C-H), 1661.95 (s, C=O), 1480 (s), 1434 (ms), 1387 (w), 1303(ms), 1262(w).

Synthesis of 2,6-dimethylacetanilide 2.



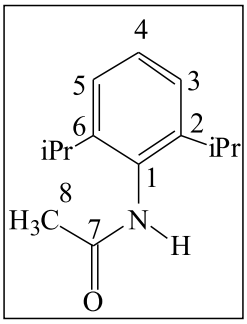
This compound was prepared in an analogous manner to the previous ligand **1**. (1.3 g, 85 %) M. p: 95 °C . ^{1}H NMR (270.16 MHz, $CDCl_3$): 2.14 (s, CH_3, 6H), 2.24 (s, CH_3, H-8, 3H), 7.07 [t, H4, ^{3}J = 7.2 Hz, 1H], 7.13 [d, H3, H5, ^{3}J = 7.2 Hz, 2H], 7.47 (bs, -NH, 1H). ^{13}C NMR (67.93 MHz, $CDCl_3$): 18.37 (CH_3), 22.93 (C8), 127.3 (C4), 128.68 (C2, C6), 135.58 (C3, C5), 169.13 (C7). IR (ATR) cm^{-1}: 3290.1 (m, NH), 2995.2 (m, C-H), 1646.0 (s, C=O), 1483 (s), 1433 (w), 1361 (s), 1261 (w), 867 (s).

Synthesis of 2,4,6-trimethylacetanilide 3.



This compound was prepared in an analogous manner to the previous ligand **1**. (1 g, 83 %) M. p: 222-224 °C. ^{1}H NMR (270.16 MHz, $CDCl_3$): 2.18 (s, CH_3, 6H), 2.20 (s, CH_3, 3H), 2.27 (s, CH_3, H8, 3H), 6.86 (s, H3, H5, 2H), 6.92 (bs, -NH, 1H). ^{13}C NMR (67.93 MHz, $CDCl_3$): 18.23 (*o*-CH_3), 20.89 (C8), 23.0 (*p*-CH_3), 129.2 (C3, C5), 135.2 (C2, C6), 169.0 (C7). IR (ATR) cm^{-1}: 3231.0 (NH), 2996.45 (m, C-H), 1643.02 (C=O), 1526.77 (s), 1487.43 (ms), 1389.82 (m), 862.56 (s).

Synthesis of 2,6-di-*iso*-propylacetanilide 4.



This compound was prepared in an analogous manner to the previous ligand **1** (*Method A*). (0.9 g, 74 %). %). ^{1}H NMR (270.16 MHz, $CDCl_3$): 2.23 (d, ^{3}J = 6.9 Hz, CH(CH_3), 12 H), 2.27 (s, CH_3, H-8, 3H), 3.44 (sept, ^{3}J = 6.8 Hz, C*H*(CH_3), 2 H), 7.23 [t, H4, ^{3}J = 7.6 Hz, 1H], 7.12 [d, H3, H5, ^{3}J = 7.5 Hz, 2H], 7.89 (bs, -NH, 1H). IR (ATR) cm^{-1}: 3268.26 (NH), 2995.6 (m, C-H), 1618.9 (C=O), 1477 (m), 1422 (m), 1359 (s), 1263 (ms), 876 (s).

Method B for compound **4**. Acetylation reactions using acetic anhydride (Ac_2O) as the reagent proceeded in excellent yields in the presence of catalytic amounts (0.5 mol %) of $TaCl_5$ at ambient temperature. To solution of 2,6-diisopropilaniline (1 g, 4.5 mmol) in Et_2O (30 ml) was treated with Ac_2O (0.42 mL, 4.5 mmol) under nitrogen atmosphere conditions at room temperature for 15 min under magnetic stirring in the presence of $TaCl_5$ (16 mg, 0.045 mmol, 1 mol%). The filtrate was washed successively with 2% aqueous NaOH (15 mL), dried ($MgSO_4$) and concentrated to afford the product (1.2 g, 95%), which was in full agreement with the mp and spectral data (IR, ^{1}H-NMR) of *method A*.

2.2. Synthesis of tin complexex

Synthesis of 5. A solution of acetanilide (2 g, 14.8 mmol) in methanol (20 mL) was electrolyzed during 3 h at 20 mA and tin were dissolved from the anode, At the end of the experiment the white solid formed was washed with cold water and ether or cyclohexane dried under vacuum. M. p. > 400° C. **IR** (ATR, cm^{-1}): 3203.76 (br, OH) 1640.33 (s, C=O), 1550 (s), 1545.9 (s), 1394.6 (s), 1297.9 (s); 1143.02 (s), 1041.1 (m), 945.2 (m), 734.6 (m), 565.9 (m).

Synthesis of 6. A similar procedure to that described above for the synthesis of complex **5**. White solid of **6**. M. p. > 400°C. **IR** (ATR, cm^{-1}): 3220.09 (br, OH), 1640.25 (s, C=O), 1558.6 (s), 1557.1 (s), 1392.5 (s), 1286.33 (s); 1143.6 (s), 1037.21 (m), 961.3 (m), 744.4 (m), 568.2 (m).

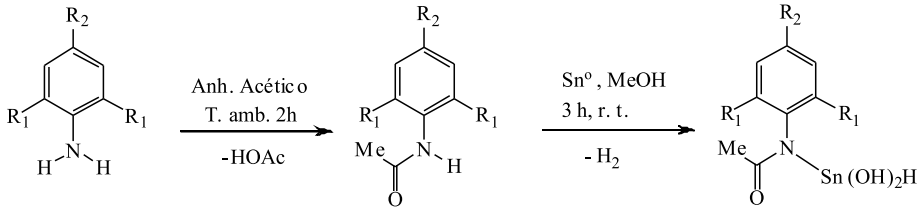
Synthesis of 7. A similar procedure to that described above for the synthesis of complex **5**. White solid of **6**. M. p. > 400° C. **IR** (ATR, cm^{-1}): 3203.03 (br, OH), 1646 (s, C=O), 1561.3 (s), 1558.7 (s), 1393.5 (s), 1292.6 (s); 1146.43 (s), 1045.4 (m), 963.6 (m), 744.3 (m), 568.1 (m). HRMS (TOF) *m/z* (%): 589.4074 (11), 355.2446 (10), 336.1486 (7, ^{124}Sn), 334.0 (7, ^{122}Sn), 332.1457 (39, ^{120}Sn), 331.1474 (14, ^{119}Sn), 330.1453 (29, ^{118}Sn), 329.1471 (11, ^{117}Sn), 328.1451 (17, ^{116}Sn), 200.1085 (9), 178.1263 (100), 149.1316 (9).

Synthesis of 8. A similar procedure to that described above for the synthesis of complex **5**. White solid of **6**. M. p. > 400°C. **IR** (ATR, cm^{-1}): 3220.19 (OH), 1623.57 (s), 1561.2 (s), 1558.9 (s), 1392.1 (s), 1298 (s); 1142.1 (s), 1042 (m), 961.2 (m), 743.5 (m), 563.3 (m).

3. Results and discussion

The compound **1** was prepared according to the literature [13]. Here, we report the synthesis of the 2,6-dimethylaniline **2**, 2,4,6-trimethylaniline **3**, and 2,6-di-*iso*-propylaniline **4** (scheme 2). The last organic ligand was synthesized by a catalyzed pathway due to the low yield [14] (*vide supra*). Compounds **1-4** were characterized by ^{1}H and ^{13}C-NMR spectroscopy.

The electrochemical method used in the synthesis of the following complexes was similar to that described in the literature [15]. The cell consisted of a tall-form beaker (50 mL) containing a methanol solution (30 mL) of the amine and a small amount of lithium perchlorate (*ca*. 10 mg.) as the supporting electrolyte. A platinum cathode and a sacrificial tin anode attached to another platinum wire served as electrodes and were connected to a *d.c*. power supply. Applied voltages of 20 mA for 3 h allowed sufficient current flow for smooth dissolution of the metal. During the electrolysis hydrogen gas was evolved at the cathode and after 3 hour of reaction. Therefore, the electrosynthesis is a promising "*green synthetic method"* in tin chemistry. The precipitate was deposited at the bottom of the cell. The solids were collected, washed with cold solution of NaOH (2 %), then with ether or cyclohexane and dried under vacuum. These solids are air-stable and moderately soluble in common organic solvents

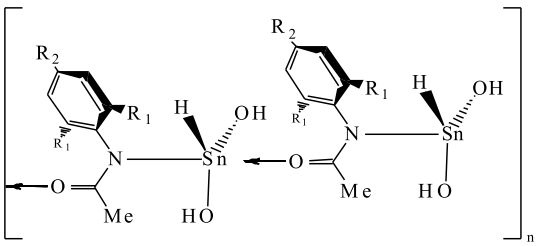


1: $R_1 = R_2 = H$
2: $R_1 = CH_3$, $R_2 = H$
3: $R_1 = R_2 = CH_3$
4: $R_1 = iPr$, $R_2 = H$

5: $R_1 = R_2 = H$
6: $R_1 = CH_3$, $R_2 = H$
7: $R_1 = R_2 = CH_3$
8: $R_1 = iPr$, $R_2 = H$

Scheme 2. Synthesis of bulky amines **1-4** and electrosynthesis of **5-8** tin complexes.

The ^{1}H NMR of compounds **1-4** exhibit resonances in the range from δ = 6.86 to 7.49 and *around 2.1 ppm a singlet was* assigned to the C*H*$_3$, thus confirming the existence of the acyl group. Also, in the range from δ = 6.92 to 8.17 the N*H* group are found as expected [16]. One interesting feature of the ^{13}CNMR spectra of **5-8**, respect to **1-4**, is the shifting to lower frequencies due to the coordination of the carbonyl group toward to the tin atom. This behavior was confirmed by the IR spectra. In compounds **5-8** IR spectra, the C=O stretching bands were shifted to lower frequencies (**5**: 1602; **6**: 1599; **7**: 1619; **8**: 1618.9 cm^{-1}) with respect to compound **1-4** (**1**: 1661; **2**: 1646; **3**: 1643; **4**: 1646 cm^{1}) due to their coordination to tin atoms. The spectra of 5-8 showed broad bands around 3200 cm^{-1}, it was assigned to OH group linked to the tin atom. Base on that, might proposed a polymeric structure though to intermolecular coordination from the carbonyl group to the tin atom (scheme 3) such as has been reported for a tin complexes derived from amines [17]. Given that compound **7** was the first to be obtained, it was possible to analyze it by means of High Performance Mass Spectrometry (figure 1). All 10 isotopes of Sn can be observed with a greater abundance of ^{120}Sn at 332.14 *m/z*. In figure 1, the most intense peak at 178.12 *m/z*, that could be corresponds to the ligand, while the peak at 332.14 *m/z* corresponds to the ligand with ^{120}Sn.



5: $R_1 = R_2 = H$
6: $R_1 = CH_3$, $R_2 = H$
7: $R_1 = R_2 = CH_3$
8: R_1 = iPr, $R_2 = H$

Scheme 3. Possible polymeric structure of tin complexes **5-8**.

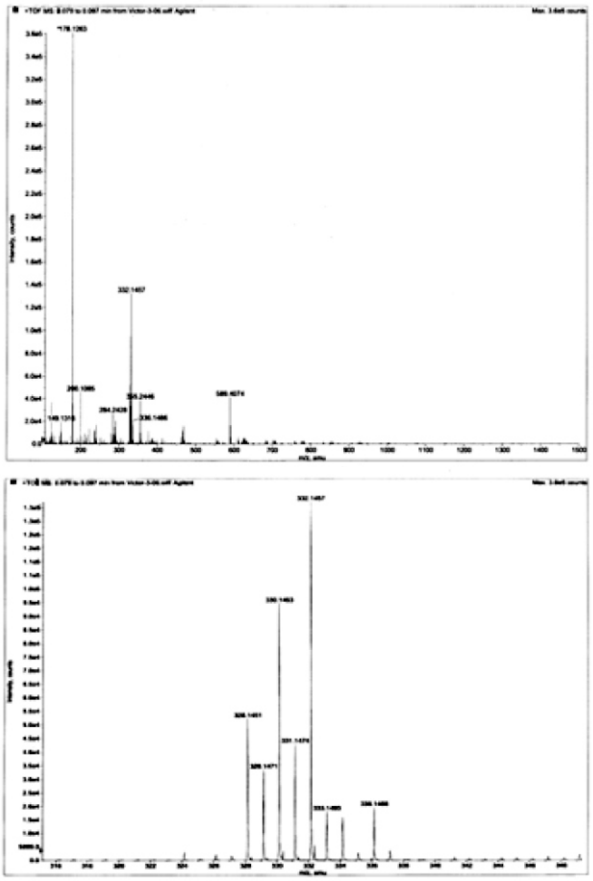


Figure 1. a) Full high-resolution mass spectrum of **7**, b) zoom of mass spectrum of **7**.

4. Conclusions

The synthesis of Sn^{IV} complexes *via* electrosynthesis was achieved which can be considering as a promising *green synthetic method*. However, the obtained compounds were different to those expected. It was observed that a polymer chain was obtained, as well as hydroxide groups directly bonded to the Sn atoms; this is because of solvent competition with the ligand, given the fact that their p*K*a is similar. Low solubility and very high melting points were likely due to the polymer chain. IR spectra provided important information on the intermolecular interactions of the carbonyl functionality.

5. References

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