

NEW HYDROGENOXALATO ADDUCTS AND MALONATO COMPLEX: SYNTHESIS AND SPECTROSCOPIC STUDIES

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Abstract: Two new hydrogenoxalato and one malonato adduct and complex have been synthesized and studied by infrared and NMR spectroscopies. The suggested structures are discrete, the hydrogenoxalate behaving as a monodentate ligand or only involved in hydrogen bonding, the environment around the tin (IV) centre being tetrahedral or trigonal bipyramidal. The malonate anion is a monodentate ligand. In all the suggested structures, when extra hydrogen bonds are considered, supramolecular architectures are obtained.

Keywords: *discrete structures, hydrogen bonds, monodentate hydrogenoxalate, monodentate malonate, supramolecular architectures, tetrahedral and trigonal bipyramidal environments*

INTRODUCTION

The organo-and halotin (IV) compounds have interesting structural aspects and applications in various fields [1 - 3]. In the dynamic of seeking new organo-and halotin(IV) compounds since a while, our group being interested both in the coordinating ability of oxyanions and organotin(IV) chemistry has published several papers [4 - 7]. For widening the data on coordinating ability of oxyanions, summarized by Hathaway [8], we have in this work allowed $\text{CyNH}_3\cdot\text{HC}_2\text{O}_4\cdot x\text{H}_2\text{O}$ to react with SnPh_3Cl or SnPh_3OH , $(\text{Bz}_2\text{NH}_2)_2(\text{CH}_2(\text{CO}_2)_2)\cdot y\text{H}_2\text{O}$ to react with SnPh_3Cl . This has yielded three new compounds, infrared and NMR studies of which have been carried out then structures suggested on the basis of spectroscopic data.

MATERIALS AND METHODS

$\text{CyNH}_3\cdot\text{HC}_2\text{O}_4\cdot x\text{H}_2\text{O}$ and $(\text{Bz}_2\text{NH}_2)_2(\text{CH}_2(\text{CO}_2)_2)\cdot y\text{H}_2\text{O}$ have been obtained as white powders on allowing the amine to react in water with the acid. The compounds **1** and **2** were obtained by mixing both as ethanolic solutions of $\text{CyNH}_3\cdot\text{HC}_2\text{O}_4\cdot x\text{H}_2\text{O}$ or $(\text{Bz}_2\text{NH}_2)_2(\text{CH}_2(\text{CO}_2)_2)\cdot y\text{H}_2\text{O}$ with SnPh_3Cl respectively in 2/1 and 1/2 ratio. The compound **3** was obtained by mixing in ethanol CyNH_2 , $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ with SnPh_3OH in 1/1/1 ratio. All the mixtures were stirred around two hours then filtered before being submitted to a slow solvent evaporation.

The analytical data [% calculated (% found)], have allowed to suggest the following formulae:

1: $2\text{CyNH}_3\text{HC}_2\text{O}_4\cdot\text{SnPh}_3\text{Cl}\cdot\text{SnPh}_3\text{OH}\cdot 2\text{CyNH}_3\text{Cl}$; % C = 54.11(54.21), % H = 6.24 (6.32), % N = 3.94 (3.83);

2: $[(\text{Bz}_2\text{NH}_2)_2\text{CH}_2(\text{CO}_2)_2]_2\cdot\text{SnPh}_3\text{Cl}\cdot 2\text{Bz}_2\text{NH}_2\text{Cl}$; % C = 70.11(69.83), % H = 6.26 (6.37), % N = 4.54 (5.22) ;

3: $\text{CyNH}_3\text{HC}_2\text{O}_4\cdot\text{SnPh}_3\text{OH}\cdot\text{H}_2\text{O}$; % C = 54.38 (54.50), % H = 5.79 (5.84), % N = 2.44 (2.65).

The elemental analyses have been obtained from the “Laboratoire de Mesures Physiques” Montpellier II University-France. The IR spectra were performed at the “Laboratorio de Espectroscopia” of the “Instituto de Química”, UNAM Mexico and at Saint Boniface College-Winnipeg-Canada. The ^1H NMR and ^{119}Sn NMR spectra were performed at the “Laboratoire de Mesures Physiques” at Montpellier II University-France. NMR spectra were recorded as saturated CDCl_3 or DMSO at room temperature, using a Bruker 300 MHz spectrometer. The ^1H and ^{119}Sn NMR were measured at 300.13 and 111.92 MHz, respectively. ^1H and ^{119}Sn NMR chemical shifts and $\delta(^{119}\text{Sn})$ NMR are given in ppm and are referred respectively to TMS and SnMe_4 all set to 0.00 ppm. The chemicals were purchased from Merck or Aldrich companies without any further purification.

RESULTS AND DISCUSSION

Let us consider the IR, ^1H NMR and ^{119}Sn NMR data of the three adducts and complex.
IR(cm^{-1}):

- 1: ν COO⁻ 1686(s), 1636.86(vs), 1583(s), ν COO⁻ 1282(s), δ COO⁻ 791(s);
 2: ν C=O 1726(vs), ν COO⁻ 1568(vs), ν COO⁻ 1286(s) 1213(m), δ COO⁻ 823(m);
 3: ν COO⁻ 1655(vs), 1541(vs), ν COO⁻ 1271(vs), δ COO⁻ 792(s).

¹H NMR(CDCl₃ or DMSO, ppm):

- 1: δ 7.26-7.74 (m, Ar-H) δ 2.9-2.96 (t, Hcyclic) δ 1.15-1.39 (m, Hcyclic);
 2: δ 9.79 (s, N-H) δ 7.41-7.70 (m, Ar-H) δ 3.33 (s, N-CH₂-Ph) δ 2.49 (s, OOC-CH₂-COO);
 3: δ 7.26-7.65 (m, Ar-H) δ 2.90 (s, Sn-OH) δ 1.26-1.28 (m, CH₂cyclic) δ 1.36-1.39 (m, CH₂cyclic) δ 1.59 (m, N-CHcyclic).

¹¹⁹Sn NMR(CDCl₃, ppm):

- 1: δ -47.05 (s), δ -82.30 (s);
 3: δ -82.28(s), δ -112.69 (s).

From these spectroscopic data, for compound **1** we have suggested two representations (Figure 1a. and Figure 1b.).

A first two hydrogen bonded components structure:

- one metallic component [Ph₃SnCl...CyNH₃...HC₂O₄...SnPh₃OH] with one hydrogen bonded SnPh₃Cl involving the cation and one hydrogen bonded SnPh₃OH involving the anion;

- one non metallic cyclic and only hydrogen bonded component [CyNH₃...HC₂O₄...CyNH₃...Cl... CyNH₃...Cl] (Figure 1a).

The NMR $\delta^{119}\text{Sn}$ values are consistent with tetrahedral SnPh₃Cl and SnPh₃OH.

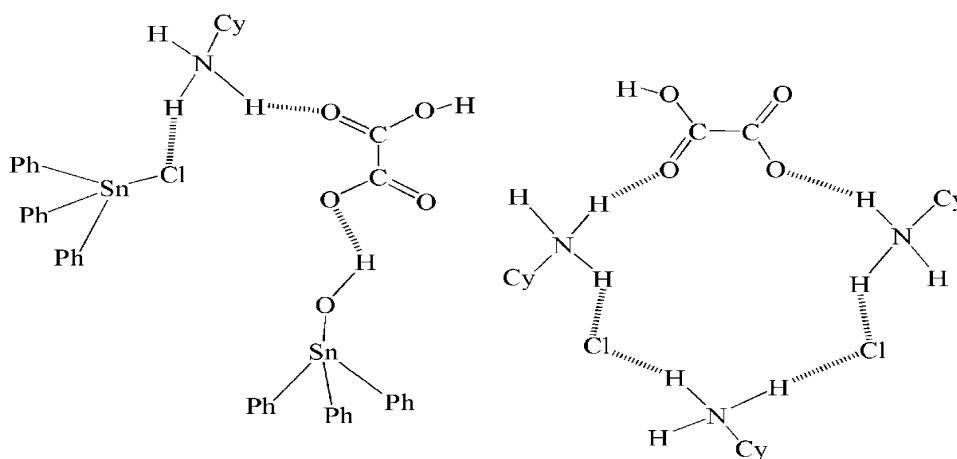


Figure 1a

The second structure is a cyclic structure in which the anions are linked via hydrogen bonds involving the cations, the SnPh₃Cl and the SnPh₃OH being lattice (Figure 1b).

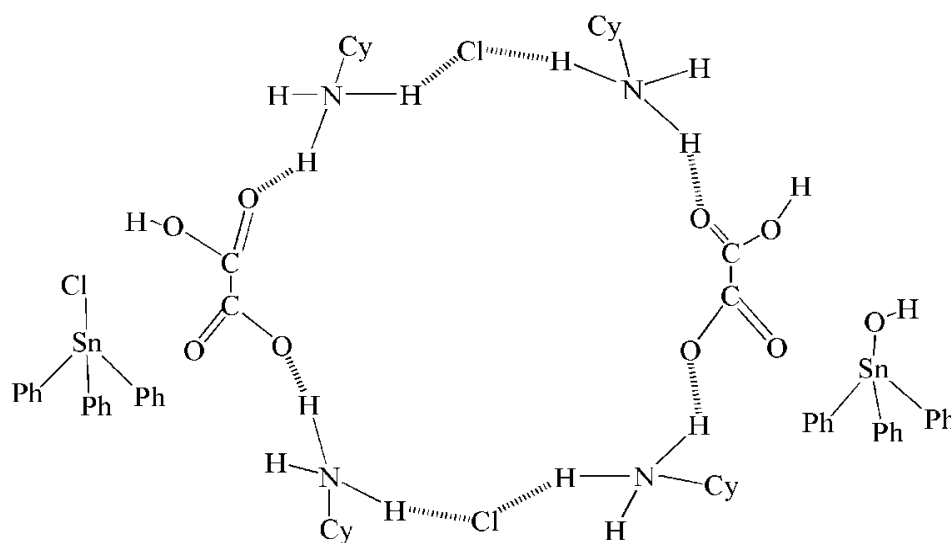


Figure 1b

Let us consider the compound **2** as $\text{SnPh}_3(\text{O}_2\text{CCH}_2\text{CO}_2)_2(\text{Bz}_2\text{NH}_2)_3 \cdot 3\text{Bz}_2\text{NH}_2\text{Cl}$. The suggested structure contains basically $[\text{SnPh}_3(\text{O}_2\text{CCH}_2\text{CO}_2)]^-$ complex-anion with a SnC_3O_2 trans trigonal bipyramidal arrangement, the two anions in apical positions being linked by a $[\text{cation} \cdots \text{Cl} \cdots \text{cation} \cdots \text{Cl} \cdots \text{cation} \cdots \text{Cl} \cdots \text{cation}]$ string, the obtained entity dimerizing through the remaining cations leading to the structure reported on Figure 2. The malonate anion behaves as a monodentate ligand.

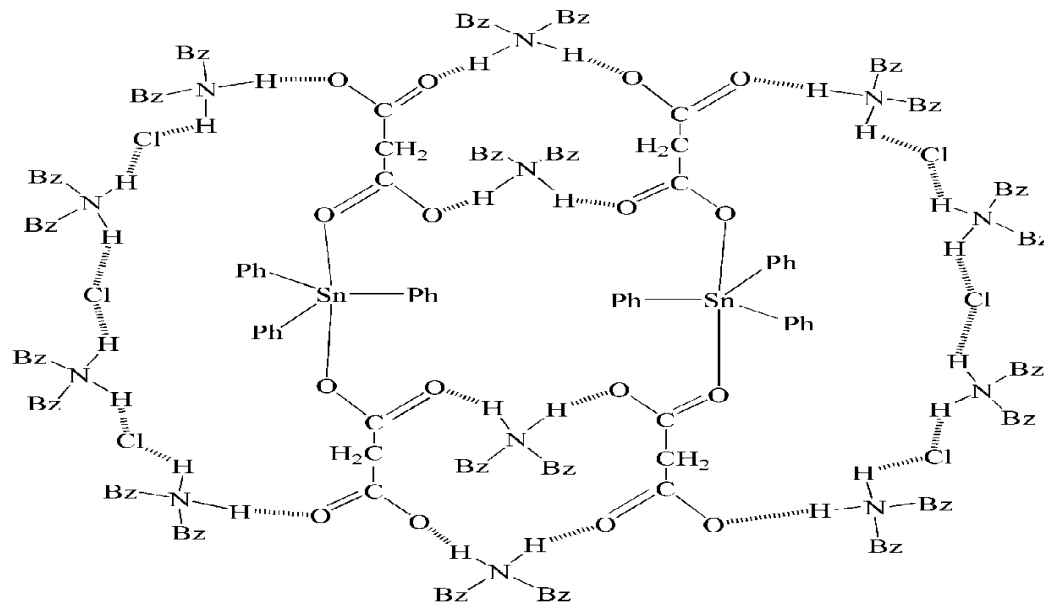


Figure 2

For **3**, the suggested structure (Figure 3) is dimeric with a $[\text{HC}_2\text{O}_4]^-$ coordinated to one SnPh_3OH (- 112. 69 ppm) while the second SnPh_3OH is hydrogen bonded to CyNH_3^+ (- 82.28 ppm): the dimerization is ensured by CyNH_3^+ cations.

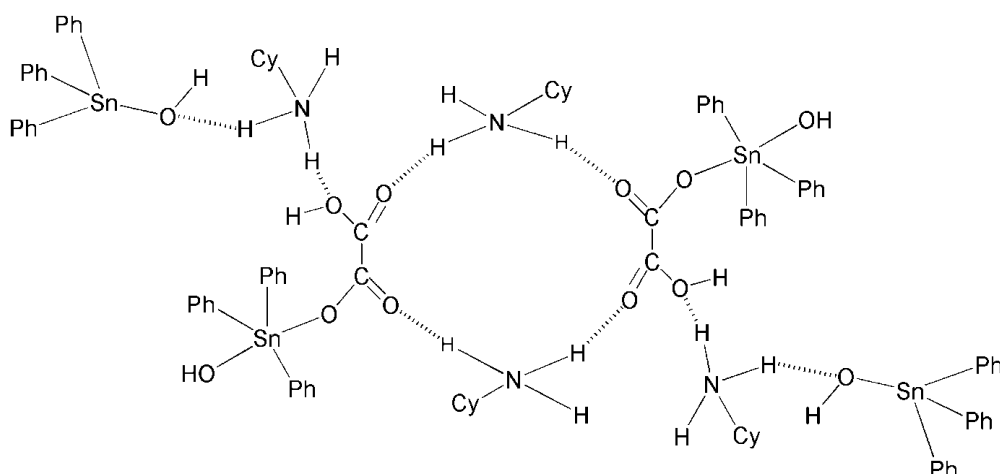


Figure 3

In hydrogenoxalate compounds the free protons of the cation and SnPh_3OH can be involved in extra hydrogen bonding leading to supramolecular architectures.

CONCLUSION

The studied adducts and complex have a discrete structure, the hydrogenoxalate anions behaving as a monodentate or a non coordinating ligand, the malonate anion being monodentate, the environments around the tin centre being tetrahedral ortrigonal bipyramidal. In the structures containing free OH or NH groups extra intermolecular hydrogen bonds can be considered leading to supramolecular architectures.

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LIST OF NOTATIONS AND SYMBOLS

IR abbreviations: vs (very strong); s (strong); m (medium). ^1H NMR and ^{119}Sn NMR abbreviations: m (multiplet), t (triplet), s (singlet).

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