Journal of Environmental Science and Engineering A 13 (2024) 207-210
doi:10.17265/2162-5298/2024.06.003

Three New Hydrogenosuccinate and Succinate Adducts Complexes: Synthesis and Spectroscopic Study

Boucar Diouf, Waly Diallo, Bocar Traoré, Daouda Ndoye, Cheikh Abdoul Khadir Diop and Mamadou Sidibé
Département de Chimie Laboratoire de Chimie Minérale et Analytique, Faculté des Sciences et Techniques, Université Cheikh Anta Diop de Dakar, Dakar 5050, Sénégal

Abstract: One new hydrogenosuccinate and two succinate adduct and complex have been synthesized and studied by infrared, UV-Visible and NMR (Nuclear Magnetic Resonance Spectroscopy) ^{119}Sn spectroscopies. The suggested structure is discrete, the hydrogenosuccinate behaving as a monodentate ligand or only involved in hydrogen bonding, the environment around the magnesium centre being triangular (compound 3). The succiate anion is a monochelating ligand (compound 1 and 2). In all the suggested structures, when extra hydrogen bonds are considered, supramolecular architectures are obtained (compound 2 and 3).

Key words: Discrete structures, hydrogen bonds, monochelating, monodentate, triangular or trigonal bipyramidal or tetrahedral environments.

1. Introduction

The organotin and metal halide compounds have interesting structural aspects and applications in various fields [1-3]. In the dynamic of seeking new organotin and metal halide compounds since a while, our group being interested both in the coordinating ability of anions and organotin(IV) chemistry has published several papers [4-7]. For widening the data on coordinating ability of anions, summarized by Hathaway [8], we have in this work allowed $EtNH_2$ or $BuNH_2$ to react with succinic acid and $SnPh_3Cl$ or $MgCl_2$ $6H_2O$ or $ZnCl_2$. This has yielded three new compounds, infrared, UV-Visible and NMR (Nuclear Magnetic Resonance Spectroscopy) studies of which have been carried out then structures suggested on the basis of spectroscopic data.

2. Materials and Methods

The compound **1** is obtained by an ethanolic solution of $EtNH_2$ with succinic acid and $SnPh_3Cl$ in 1/1/2 ratio. The compounds **2** is obtained by mixing an ethanolic + water solution of $BuNH_2$ with succinic acid and $ZnCl_2$ in the 1/2/1 ration and the compound **3** is obtained by a methanolic solution of $EtNH_2$ with succinic acid and $MgCl_2{\cdot}6H_2O$ in the ratio 2/2/2. All the mixtures gave limpid solution (compounds **2** and **3**) or white precipitate (compound **1**) after 3 h of reflux at 60 ℃ and have been submitted to a slow solvent evaporation. The analytical data allow suggesting the following formulae (Table 1).

The elemental analyses have been obtained from the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France. The ^{119}Sn NMR spectra were performed at the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France using a Bruker Avance 400 MHz Spectrometer with a low sensitivity band. The IR spectra of the compounds were recorded at room temperature using an FTIR (Fourier Transform Infrared) spectrometer at the University Cheikh Anta Diop Dakar and at the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France (over a range from 4,500 to 400 cm^{-1}) in the form of suspension of powders in Nujol or crushed dry. The UV-visible spectroscopies have been obtained from the spectrometer at the University Cheikh Anta Diop Dakar.

Corresponding author: Boucar Diouf, Ph.D., research fields: molecular chemistry.

Table 1 Suggested formulae of synthesized compounds and the elemental analyses.

Compound	Chemical formulae	Elemental analyses (%)					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
1	$(EtNH_3)[C_4H_4O_4(SnPh_3)]$ $SnPh_3Cl$	56.20	56.71	4.72	4.11	1.56	1.50
2	$(BuNH_3)_2[C_4H_4O_4(ZnCl_2)]$ H_2O	34.42	34.12	7.22	7.07	6.69	6.20
3	$(EtNH_3)_2[(C_4H_5O_4)_2(MgCl_2)_2]$	27.89	27.83	5.07	5.12	5.42	5.40

3. Results and Discussion

Let us consider the IR, ^{119}Sn NMR and UV-visible data. IR (cm^{-1}): 1: ν(NH) = 2,935 (br); νas (COO^-) = 1,634 (m), 1,538 (vs); νs (COO^-) = 1,438 (s), 1,380 (vs); δ(COO^-) = 894 **(**s), 869 (s); νas (SnPh3) = 774 (vs), 690 (s) 2: ν(NH) = 2,975 (br); ν(OH) = 3,411 (br); δ(NH) = 1,511 (vs); δ(OH) = 1,301 (vs); νas (COO^-) = 1,634 (s), 1,473 (s); νs (COO^-) = 1,399 (s), 1,375 (vs); δ(COO^-) = 895 (w); 840 (w); ν(Zn-O) = 594 (m); 3: ν(NH) = 2,925 (br); ν(OH) = 3,050 (br); δ(NH) = 1,537 (s); δ(OH) = 1,310 (vs); νas (COO^-) = 1,587 (m), 1,485 (vs); νs (COO^-)= 1,443 (m); 1,388 (vs); δ(COO−) = 845 (m), 801 (m); ν(Mg-O) = 589 (s); ^{119}Sn NMR(CDCl3, ppm): 1: δ = -170.21(s), -47(s); UV-visible (nm): 1: λmax = 291(vs); 2: λmax = 292(vs).

From these spectroscopic data, we have suggested three compounds.

*3.1 $(EtNH_3)[C_4H_4O_4(SnPh_3)]\cdot SnPh_3Cl$ (**1**)*

While considering the IR of the compound **1** derivative, the doublet at 727 and 692 cm^{-1} attributed to phenyl vibrations confirming the presence of the $SnPh_3$ residue. The broad band centered at 2,930 cm^{-1} confirms the presence of cation $EtNH_3^+$. Several succinate bands appear, including the one at 1,538 cm^{-1} which strongly confirms its presence. The ^{119}Sn NMR spectrum shows a signal at δ = -170 ppm in agreement with a pentacoordinated tin atom [9] and another signal at δ = -47 ppm characteristic of a free $SnPh_3Cl$ molecule [10].

The only strong absorption at 291 nm assigned to n→π* transitions, reflects the mesomeric effect observed on the free oxygen doublets of succinate. From these spectroscopic data, the structure proposed for the compound is formed of two parts, an $EtNH_3C_4H_4O_4SnPh_3$ complex in which the tin atom is pentacoordinated. The other part is formed of a free $SnPh_3Cl$ molecule. The whole forms a discrete structure in which the succinate anion is monochelating, the environment around the tin is cis-pentacoordinated and an isolated tetrahedral $SnPh_3Cl$ residue (Fig. 1).

*3.2 $(BuNH_3)_2[C_4H_4O_4(ZnCl_2)]\cdot H_2O$ (**2**)*

On the infrared spectrum, the broad band centered at 2,975 cm^{-1} confirms the presence of hydrogen bonds via the $BuNH_3^+$ cation and that at 3,411 cm^{-1} confirms the presence of water molecules. Several bands in the valence zone of the succinate, including the one at 1,634 cm^{-1} which appears strong, confirm its presence. At medium frequency the average band at 596 cm^{-1} confirms the presence of Zn—O bond [11]. The only strong absorption at 292 nm assigned to n→π* transitions, reflects the mesomeric effect observed on the free oxygen doublets of succinate. For compound (**2**) the suggested structures are discrete (Fig. 2), the environment around the copper centre being tetrahedral and the salicylate behaving as a monochelating ligand. When the cation is involved through NH…Cl hydrogen bonds a supramolecular architecture may be obtained [12]. Water molecules are in a network.

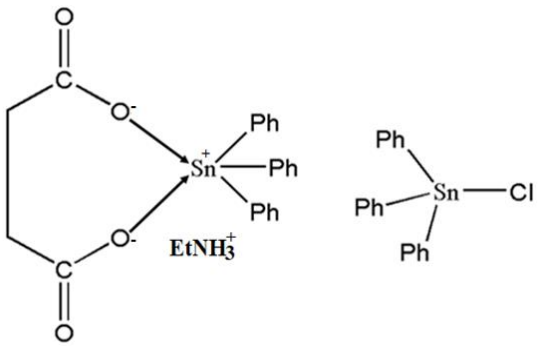

Fig. 1 Proposed structure for the compound 1.

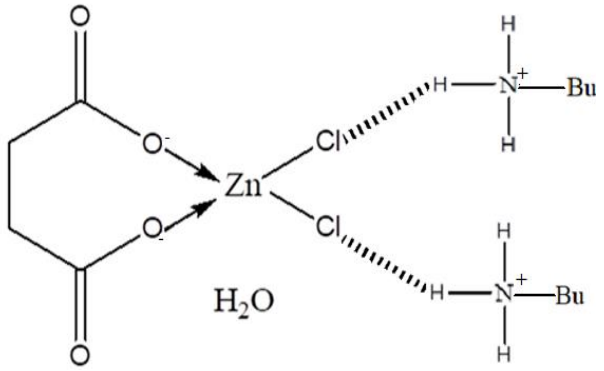

Fig. 2 Proposed structure for the compound 2.

*3.3 $(EtNH_3)_2[(C_4H_5O_4)_2(MgCl_2)_2]$ (**3**)*

On the infrared spectrum, the broad band centered at 2,925 cm^{-1} confirms the presence of hydrogen bonds via the $EtNH_3^+$ cation and that at 3,050 cm^{-1} confirms the presence of the OH group of hydrogenosuccinate. At strong frequency the average band at 589 cm^{-1} confirms the presence of Mg—O bond [13]. Several bands in the valence zone of the succinate, including the one at 1,485 cm^{-1} which appears very strong, confirm its presence. Through these IR data, we propose a discrete structure in which the hydrogenosuccinates are monodentate and the environment around each magnesium is triangular. The cation is involved via N-H…..O type hydrogen bonds and ensures the good stability of the compound (Fig. 3).

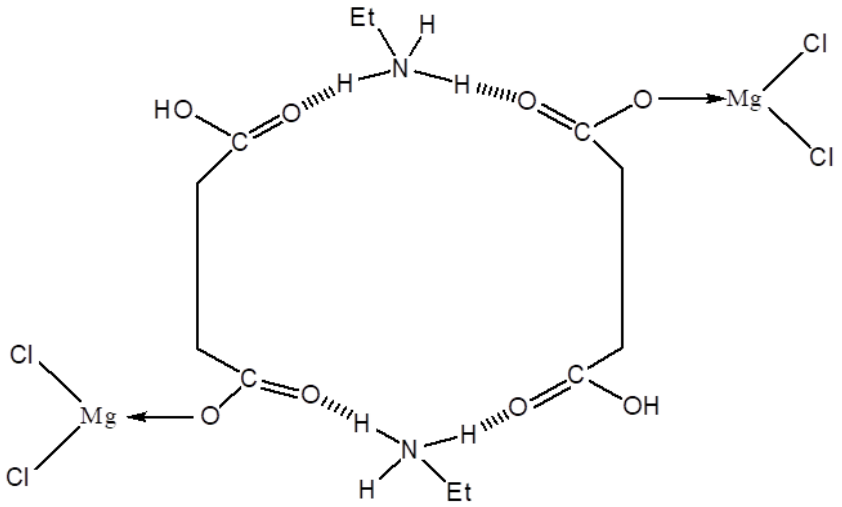

Fig. 3 Proposed structure for the compound 3.

4. Conclusion

The studied adducts and complex have a discrete structure, the hydrogenosuccinate anions behaving as a monodentate ligand, the succinate anion being monochelating. The environments around the tin center are tetrahedral or trigonal bipyramidal. The environment around the zinc being tetrahedral and the environment of magnesium is triangular. In the structures containing free OH or NH groups extra intermolecular hydrogen bonds can be considered leading to supramolecular architectures.

List of Notations

IR abbreviations: Br (Broad), (VS) Very Strong, (S) Strong, (M) Medium, (W) Weak.

Acknowledgements

We thank Laurent Plasseraud, ICMUB UMR CNRS 6302, University of Burgundy,Faculty of Sciences, Dijon, France.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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