

SOME NEW SULFONATO ADDUCT: SYNTHESIS AND SPECTROSCOPIC STUDIES

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Received: May, 23, 2014

Accepted: October, 10, 2014

Abstract: Three new adducts have been synthesized and studied by infrared and NMR spectroscopies. The suggested structures are discrete with a pyridine -3- sulfonate acting as a tri O-chelating and N-donor or as a non σ coordinating ligand, a 4-aminobenzenesulfonate behaving as a monodentate O-donor, the environments around the tin centre being tetrahedral, octahedral or seven coordinated. In all the studied compounds, supramolecular architectures are obtained when hydrogen bonds are considered.

Keywords: *discrete structures, hydrogen bonds, monodentate 4-aminobenzenesulfonate, octahedral, seven coordinated environments, supramolecular architectures, tetrahedral, tri O-chelating and N-donor pyridine -3 - sulfonate*

INTRODUCTION

Substituted and non substituted anions are known to coordinate very well transition and non transition metals as reported by Hathaway [1]. Since several decades our group is focusing in the coordinating ability of oxyanions and has published several papers [2-5]. As a continuation of that research we have initiated in this work the study of the interactions between $(\text{Bu}_2\text{NH}_2)\text{Py-3-SO}_3$ and SnBu_2Cl_2 or $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ which have yielded three new adducts, infrared and NMR studies of which have been carried out then structures suggested on the basis of infrared data.

MATERIALS AND METHODS

The compound **1** is obtained by allowing an ethanolic solution of $(\text{Bu}_2\text{NH}_2)\text{Py-3-SO}_3$ – obtained as a powder on allowing Bu_2NH to react with pyridine-3-sulfonic acid in water and allowing the water to evaporate in the oven at 60°C to react in 1/1 ratio with an ethanolic solution of SnBu_2Cl_2 , while compounds **2** and **3** were obtained by mixing ethanolic solutions of $(\text{Bu}_2\text{NH}_2)\text{Py-3-SO}_3$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 2/1 ratio (**2**), ethanolic solutions of $\text{CyNH}_3\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3$ and ZnBr_2 in 1/1 ratio (**3**). 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 (Table 1).

Table 1. Suggested formulae of the synthesized compounds

Comp	Suggested formulae	Chemical composition (% mass)					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
1	$\text{Py-3-SO}_3\text{Bu}_2\text{NH}_2 \cdot 3/2\text{SnBu}_2\text{Cl}_2$	40.35	41.06	6.86	7.12	3.76	3.84
2	$4\text{Py-3-SO}_3\text{Bu}_2\text{NH}_2 \cdot \text{SnCl}_4 \cdot 2\text{EtOH}$	44.90	45.18	7.21	6.56	4.9	7.69
3	$\text{CyNH}_3\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3 \cdot \text{ZnBr}_2 \cdot \text{H}_2\text{O}$	27.95	27.29	4.30	4.13	5.43	5.68

The elemental analyses have been obtained from the “Laboratoire de Mesures Physiques” Montpellier II University (France). The IR spectra were performed at the University of Saint Boniface-Winnipeg (Canada). The IR data are given in cm^{-1} [abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak]. The ^1H NMR analyses were performed at the “Laboratoire de Mesures Physiques” at Montpellier II University. NMR spectra were recorded as saturated CDCl_3 or DMSO at room temperature, using a Bruker 300 MHz spectrometer. The ^1H was measured at 300.13 MHz. ^1H chemical shifts NMR are given in ppm and are referred respectively to TMS [NMR abbreviation: m (multiplet)].

All the chemical were from ALDRICH Company and used as received.

RESULTS AND DISCUSSION

Let us consider the IR data in cm^{-1} of the three adducts.

1: $\nu_{\text{as}}(\text{SO}_3)$: 1257 (s), 1209 (s), 1187 (s), 1143 (s); $\nu_{\text{s}}\text{SO}_3$: 1043 (s), 1022 (s); $\nu(\text{C-S})$: 742 (s); $\delta(\text{SO}_3)$: 875 (s), 821 (w), 777 (s), 683.17 (s), 632 (s); $\nu_{\text{as}}(\text{SnBu}_2)$: 611 (vs);

2: $\nu_{\text{as}}(\text{SO}_3)$: 1200 (s), 1176 (s); $\nu_{\text{s}}(\text{SO}_3)$: 1043 (s); $\nu(\text{C-S})$: 745 (s); $\delta(\text{SO}_3)$: 632 (m);

3: $\nu_{\text{as}}(\text{SO}_3)$: 1243 (vs), 1163 (vs), 1122 (vs); $\nu_{\text{s}}(\text{SO}_3)$: 1085 (vs), 1036 (vs), 1012 (s); $\nu(\text{C-S})$: 694 (s); $\delta(\text{SO}_3)$: 616 (w), 580 (s).

It seems worthy to outline the absence of the bands at 683 cm^{-1} and 611 cm^{-1} due to SnBu_2 on the spectrum of **2**. The intensity of the band at 611 cm^{-1} indicates non linear SnBu_2 group.

Let us consider the ^1H NMR (CDCl_3 or DMSO, ppm) data of adducts **1** and **2**.

1: δ 7.34-7.92 (m, C- H_{Py}), δ 8.44-8.74 (m, NH_2);

2: δ 7.60-7.81 (m, C- H_{Py}), δ 8.39-8.90 (m, NH_2) (the ^{119}Sn NMR spectra being taken in DMSO, the solvent coordinates the complex; so the NMR data cannot be correlated with the suggested structure).

From these spectroscopic data, we suggest:

For **1** we suggest a dimeric structure (Figure 1) with a pyridine-3-sulfonate anion tri-O-chelating and N-donor, the environment around the tin centre being octahedral or seven coordinated.

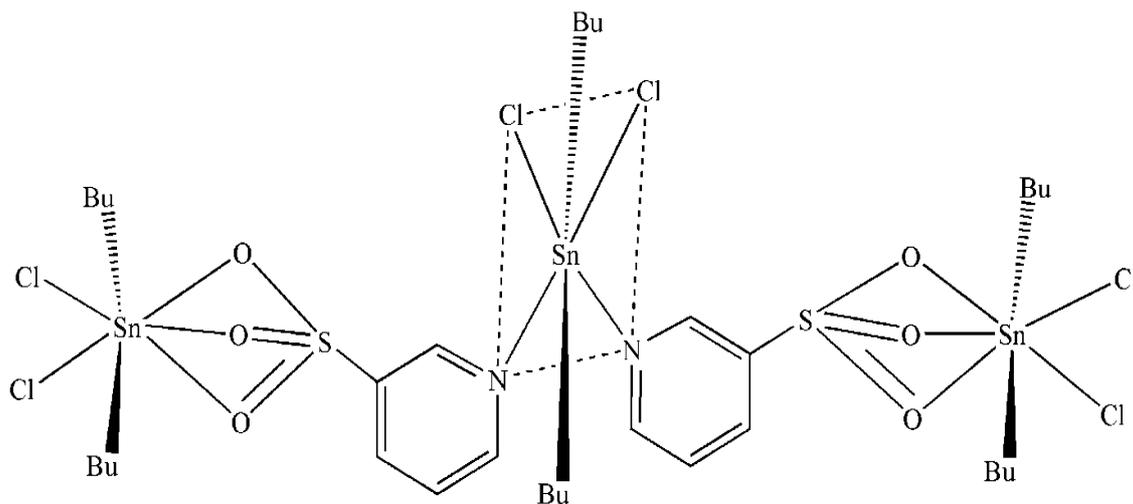


Figure 1. Proposed structure for the compound **1**

For **2** the suggested structures are discrete with a SnCl_4 molecule coordinated by two ethanol molecules conferring an octahedral environment around the tin centre, the $\text{SnCl}_4 \cdot 2\text{EtOH}$ adduct interacting through $\text{OH} \dots \text{N}$ hydrogen bonds with the dimeric cycles of $\text{Bu}_2\text{NH}_2\text{Py-3-SO}_3$ (Figure 2a) or $\text{NH} \dots \text{Cl}$ hydrogen bonds with $\text{Bu}_2\text{NH}_2\text{Py-3-SO}_3$ (Figure 2b).

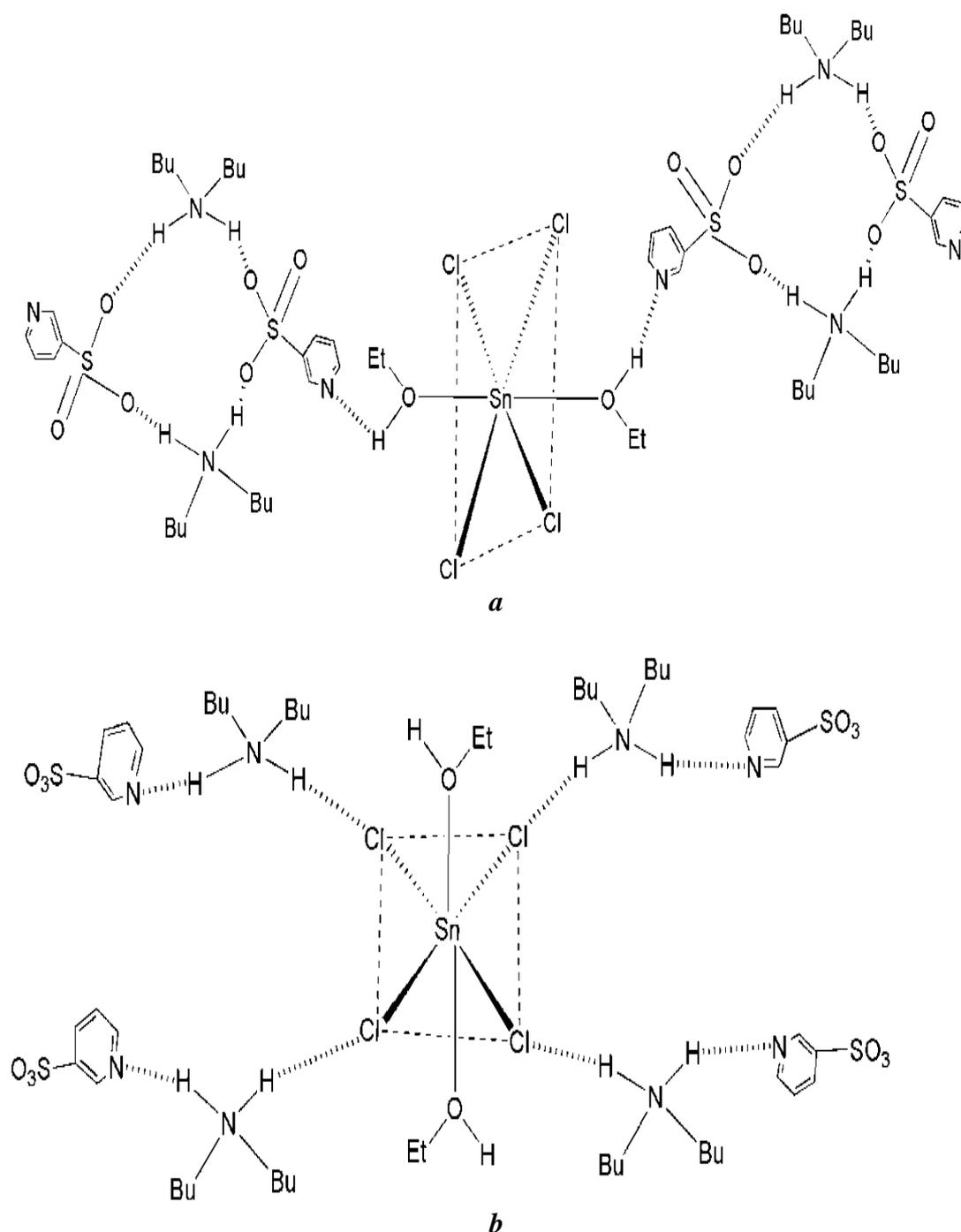


Figure 2. Proposed structure for the compound **2**

For **3** we suggest a dimeric structure with a monodentate O-donor, the dimerization involving the cations through NH...O hydrogen bonds, the environment around the zinc being tetrahedral (Figure 3).

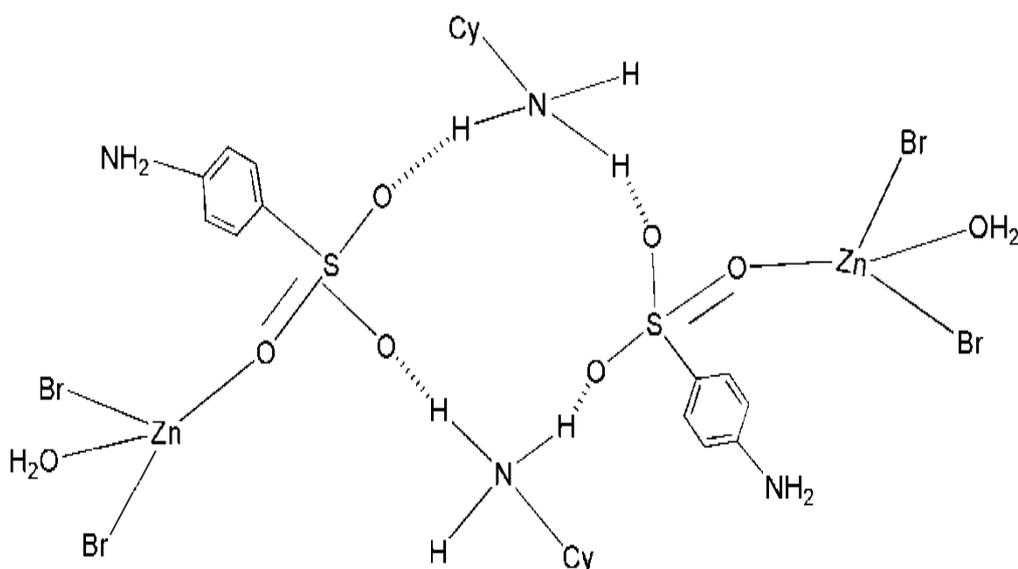


Figure 3. Proposed structure for the compound 3

For all the studied compounds the cations can be involved in extra hydrogen bonds leading to a supramolecular architecture.

CONCLUSION

All the studied adducts have a discrete structure, the sulfonate as a tri O-chelating/N-donor or O-donor ligand, the environment around the metallic centres being tetrahedral, octahedral or seven coordinated. When extra intermolecular hydrogen bonds are considered supramolecular architectures are obtained.

ACKNOWLEDGEMENTS

We thank Professor L. A. DIOP (Saint-Boniface College –Winnipeg, Canada) and Dr Cea Olivares R. (“Laboratorio de Espectroscopía” of the “Instituto de Química”, UNAM -Mexico) for equipment support.

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