

**$(\text{Cy}_2\text{NH}_2)_2\text{SO}_4 \cdot 2\text{SnMe}_3\text{SO}_4\text{Cy}_2\text{NH}_2$;
 $2(\text{Cy}_2\text{NH}_2)_2\text{SO}_4 \cdot 5\text{SnMe}_3\text{SO}_4\text{Cy}_2\text{NH}_2$;
SYNTHESIS AND INFRARED STUDY**

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Abstract: Allowing $(\text{Cy}_2\text{NH}_2)_2 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Cy}_2\text{NH}_2 \cdot \text{HSO}_4$ to react with SnMe_3Cl in ethanolic media in two specific ratios the sulphato complexes (mentioned in this paper title) were obtained and their infrared study was carried out. Discrete structures containing the complex-anion $[\text{SO}_4(\text{SO}_4\text{SnMe}_3)_2]^{4-}$ consisting of a central bidentate sulphate linked to SnMe_3 groups which are then coordinated to monodentate sulphate anions or the complex-anion $[(\text{SO}_4)_6(\text{SnMe}_3)_5]^{7-}$ consisting of planar SnMe_3 groups, monodentate or bidentate sulphate anions, these complex-anions dimerizing through cations via hydrogen bonds, are suggested.

Keywords: *coordinating sulphate, dimeric structures, $\text{NH}\dots\text{O}$
hydrogen bonds, planar SnMe_3 residue, tin (IV)
polynuclear complex-anion*

INTRODUCTION

The organotin (IV) molecules are known as wood preservatives, anti fouling paints, drugs, etc. [1]. This is why several groups including our [2-9] have been focusing on the synthesis of new compounds of this family.

In this paper we have initiated the study of the interactions between $(\text{Cy}_2\text{NH}_2)_2\cdot\text{SO}_4\cdot 2\text{H}_2\text{O}$ or $\text{Cy}_2\text{NH}_2\text{HSO}_4$ and SnMe_3Cl which has yielded the two studied complexes, infrared study of each complex was carried out, then structures were suggested on the basis of the infrared data.

MATERIALS AND METHODS

By mixing amino-immino-methanesulphonic and sulphuric acids with dicyclohexylamine both in 1/1 ratio in water and after a solvent evaporation at 60 °C, crystals of $(\text{Cy}_2\text{NH}_2)_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ (**L₁**) (notice the cleavage of C-S bond of amino-immino-methane sulphonic acid leading to a sulphate) and a powder of $\text{Cy}_2\text{NH}_2\text{HSO}_4$ (**L₂**) were obtained according to elemental analyses: [% found (% calculated)]:

- **L₁**: C 57.98(58.03); H: 10.52(10.55); N: 5.60(5.64);
- **L₂**: C: 51.64(51.59); H: 8.97(9.02); N: 4.97(5.01).

When ethanolic solutions of $(\text{Cy}_2\text{NH}_2)_2\cdot\text{SO}_4\cdot 2\text{H}_2\text{O}$ and $\text{Cy}_2\text{NH}_2\text{HSO}_4$ are mixed with ethanolic solutions of SnMe_3Cl in 1/1 ratio and 1/2 ratio respectively, clear solutions are obtained and stirred for two hours. When submitted to a slow solvent evaporation, these solutions yield respectively white crystals and a white powder which elemental analyses data have allowed to suggest the following formulae.

Elemental analyses [% found (% calculated)]:

for **A₁**: % **C**: 48.22 (48.04); % **H**: 8.54 (8.94); % **N**: 4.17 (5.39) and for **A₂**: % **C**: 47.16 (47.36); % **H**: 8.40 (8.54); % **N**: 4.02 (4.95) allowed us to suggest the following formulae: $(\text{Cy}_2\text{NH}_2)_2\text{SO}_4\cdot 2\text{SnMe}_3\text{SO}_4\text{Cy}_2\text{NH}_2$ and $2(\text{Cy}_2\text{NH}_2)_2\text{SO}_4\cdot 5\text{SnMe}_3\text{SO}_4\text{Cy}_2\text{NH}_2$.

The elemental analyses were performed by the Department of Chemistry, University of Bath (UK). The infrared spectra were recorded by a FTIR-Nicolet (4000-400 cm^{-1}) spectrometer at the University of Addis Ababa (Ethiopia), the sample being as Nujol mulls, using CsI windows. Infrared data are given in cm^{-1} – IR abbreviations: (br) broad (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (w) weak, (vw) very weak. All the chemicals were purchased from Aldrich and used without any further purification.

RESULTS AND DISCUSSION

Let us consider the infrared data (cm^{-1}) of:

- **A₁**: [$\nu_3(\text{SO}_4)$: 1204sh, 1192sh, 1119vs, 1067sh, 1053sh; $\nu_1(\text{SO}_4)$: 972w, 956w; $\nu_4(\text{SO}_4)$: 670w, 619s, 592m; $\nu_{\text{as}}(\text{SnC}_3)$: 548w];
- **A₂**: [$\nu_3(\text{SO}_4)$: 1151s, 1101s, 1051s; $\nu_1(\text{SO}_4)$: 990w; $\nu_4(\text{SO}_4)$: 629m, 616m, 602w; $\nu_2(\text{SO}_4)$: 446w; $\nu_s(\text{SnC}_3)$: 516tr; $\nu_{\text{as}}(\text{SnC}_3)$: 550m].

The basic structure of **A₁** while considering the complex-anion $[\text{SO}_4(\text{SO}_4\text{SnMe}_3)_2]^{4-}$ consists of a central bidentate sulphate linked to SnMe_3 groups to which are then

coordinated two monodentate sulphate anions. This entity dimerizes through cations by means of N-H...O bonds (Figure 1).

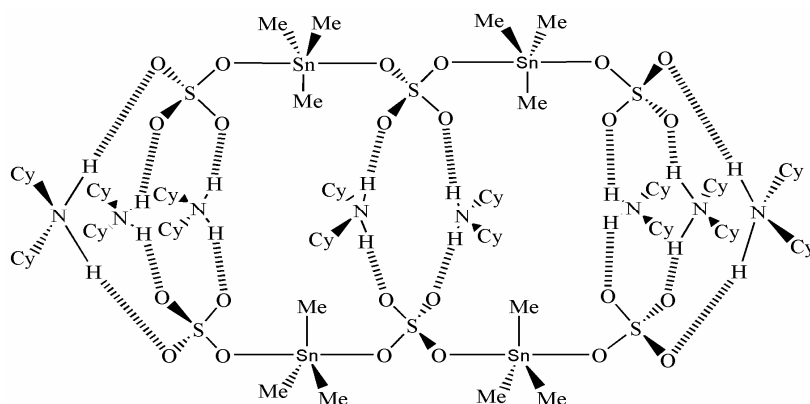


Figure 1. Suggested structure for A_1

For the second complex, the suggested structure is a tetramer in which each monomer complex-anion $[(SO_4)_6(SnMe_3)_5]^{7-}$ consisting of planar $SnMe_3$ groups, monodentate or bidentate sulphate anions dimerizes through cations by means of NH...O hydrogen bonds, these dimers dimerizing and leading to a tetramer (Figure2).

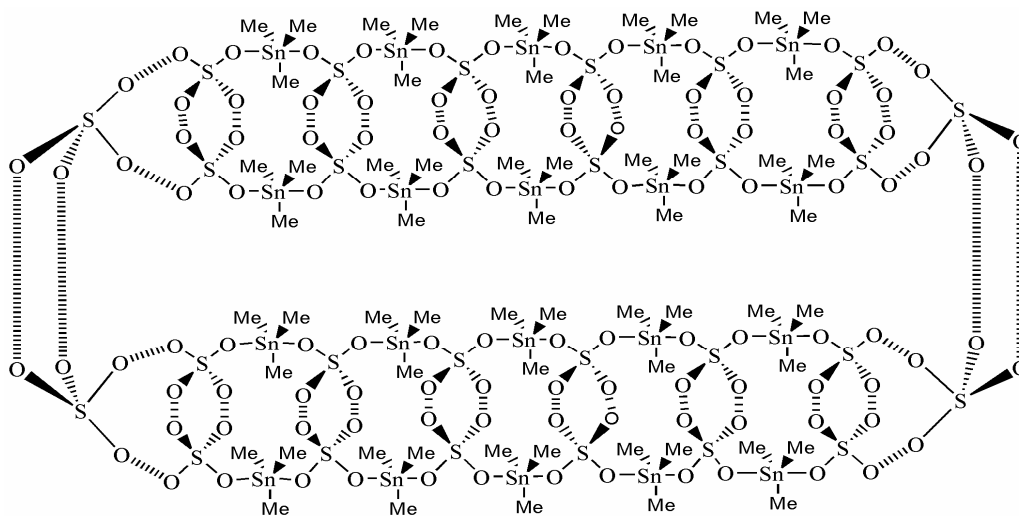


Figure 2. Suggested structure for A_2

NB: In Figure 2 dashed lines indicate hydrogen bonded cations.

The appearance of $\nu_1(SO_4)$ and $\nu_2(SO_4)$ bands as very weak bands indicate a Td symmetry for the sulphate for the two studied complexes. The broad absorption around 2900 cm^{-1} allows concluding to the presence of N-H...O hydrogen bonds. The appearance of $\nu_s(SnMe_3)$ band as a very weak band at 516 cm^{-1} shows planar $SnMe_3$ groups according to Group Theory.

CONCLUSIONS

The two studied adducts have discrete structure (dimeric and tetrameric); the tin centre is in a pentagonal environment, the sulphate being mainly bidentate. Macromolecules have been obtained due to the presence of cations involved in hydrogen bonds.

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