

MOLYBDATO ORGANOTIN (IV) ADDUCTS AND COMPLEXES: SYNTHESIS AND INFRARED STUDY

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Abstract: Nine new molybdato adducts and complexes have been synthesized and studied by infrared spectroscopy. The suggested structures are discrete or infinite chain, the molybdate behaving as a bidentate, mono-, bi- or tetrachelating ligand, the environment around the tin (IV) centre being octahedral or trigonal bipyramidal. In water containing compounds, when extra intermolecular O-H...O or O-H...Cl hydrogen bonds are considered, supramolecular architectures may be obtained.

Keywords: *bichelating, bidentate, monochelating and monodentate or tetrachelating molybdate, discrete or infinite chain structures, octahedral environment, supramolecular architectures*

INTRODUCTION

The data on the coordinating ability of oxyanions have been reviewed in [1]. Several papers dealing with have yet been published from our laboratory [2 – 8]. The data on molybdate anion acting as ligand as scarce according to Cambridge data 2014 compared to polymolybdate anions [9 – 11]. Our group has yet published some papers dealing with the molybdate anion behaving as ligand [12 – 14]. For widening the data on the molybdate anion and for seeking new complexes with a biological activity [15], we have allowed in this work $(\text{MEIH})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ (MEI = methyl-2-imidazole) to react with SnBu_2Cl_2 , SnBuCl_3 , SnCl_4 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ or SnPh_3Cl . This has yielded nine new compounds, infrared study of which has been carried out then structures suggested on the basis of infrared data.

MATERIALS AND METHODS

$(\text{MEIH})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ [% calculated (% found): % C = 27.92 (28.03), % H = 4.69 (4.82), % N = 16.28 (16.19)] has been obtained as a white powder on allowing MEI to react in water with molybdic acid. The compounds **1**, **2** and **3** were obtained as bluish (**1** and **3**) or yellow (**2**) powders on allowing in acetonitrile $(\text{MEIH})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ to react with SnBuCl_3 in 2/1 ratio for **1** and 1/2 ratio for **2**, SnCl_4 in 2/1 ratio for **3** while the compounds **4** and **7** were obtained as white powders by mixing in acetonitrile $(\text{MEIH})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ and SnBuCl_3 or SnCl_4 in 1/1 ratio.

The compounds **5**, **6**, **8** and **9** were obtained as brown (**5** and **8**) or white (**6** and **9**) on allowing in methanol $(\text{MEIH})_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ to react with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ -1/1 ratio (**5**) or 2/1 ratio (**8**)-, SnPh_3Cl in 2/1 ratio for **6** or SnBu_2Cl_2 in 1/1 ratio for **9**.

All the mixtures were stirred around two hours before being submitted to a slow solvent evaporation.

The analytical data have allowed to suggest the following formulae (Table 1).

Table 1. Results of the elemental analyses of compounds 1-9

| Compound | Chemical formula | Elemental analysis [%] | | | | | |
|----------|--|------------------------|-------|-------|-------|-------|-------|
| | | C | | H | | N | |
| | | calc. | found | calc. | found | calc. | found |
| 1 | $(\text{MEIH})_2\text{MoO}_4 \cdot 4\text{SnBuCl}_3$ | 19.81 | 19.91 | 3.46 | 3.57 | 3.85 | 3.91 |
| 2 | $\text{Sn}(\text{MoO}_4)_2(\text{CH}_3\text{CN})_2$ | 9.23 | 9.40 | 1.16 | 1.26 | 5.38 | 5.37 |
| 3 | $(\text{MEIH})_2\text{MoO}_4 \cdot 2\text{SnCl}_4 \cdot 1/4(\text{MEIH})_2\text{MoO}_4$ | 12.93 | 12.84 | 1.90 | 2.00 | 7.54 | 7.60 |
| 4 | $(\text{MEIH})_2\text{MoO}_4 \cdot \text{SnBu}_2\text{MoO}_4 \cdot 2\text{SnBuClMoO}_4$ | 19.72 | 19.67 | 3.45 | 3.54 | 3.83 | 3.87 |
| 5 | $\text{SnCl}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} \cdot 1/6(\text{MEIH})_2\text{SnCl}_6$ | 3.42 | 3.53 | 1.36 | 1.40 | 1.99 | 2.03 |
| 6 | $(\text{MEIH})_2\text{MoO}_4 \cdot 2\text{SnPh}_2\text{MoO}_4$ | 32.25 | 31.94 | 2.88 | 2.82 | 4.70 | 4.65 |
| 7 | $3(\text{MEIH})_2\text{MoO}_4 \cdot 2\text{SnCl}_4$ | 19.22 | 19.13 | 2.82 | 2.85 | 11.21 | 11.29 |
| 8 | $(\text{MEIH})_2\text{MoO}_4 \cdot 2\text{SnCl}_2\text{MoO}_4 \cdot \text{Sn}(\text{MoO}_4)_2$ | 6.56 | 6.45 | 0.96 | 1.09 | 3.83 | 3.94 |
| 9 | $2(\text{MEIH})_2\text{MoO}_4 \cdot \text{SnBuCl}_3 \cdot 2\text{Sn}(\text{MoO}_4)_2$ | 13.26 | 13.15 | 2.06 | 2.03 | 6.19 | 6.07 |

The elemental analyses have been obtained from “The Microanalyses Laboratory” University of Burgundy-Dijon-France. The IR spectra were performed at the University of Burgundy-Dijon-France using a Bruker FTIR spectrometer.

IR abbreviations: vs (very strong); s (strong); m (medium), w (weak), vw (very weak), sh (shoulder). The chemicals were purchased from Aldrich Company-Germany without any further purification.

RESULTS AND DISCUSSION

Let us consider the main IR data (in cm^{-1}) of the studied adducts and complexes. The assignments are based on Nakamoto [16].

1: νMoO_4^{2-} : 983 (s), 921 (s), 870 (m), 801 (m), 753 (w); δMoO_4^{2-} : 679 (m), 612 (vw), 540 (m);

2: νMoO_4^{2-} : 954 (vs), 919 (sh), 870 (m), 761 (s); δMoO_4^{2-} : 683 (s), 572 (m);

3: νMoO_4^{2-} : 986 (s), 944 (m), 859 (m), 733 (vs); δMoO_4^{2-} : 679 (vs), 652 (m), 566 (w), 508 (w);

4: νMoO_4^{2-} : 982 (s), 920 (vs), 869 (m), 752 (m); δMoO_4^{2-} : 678 (m), 613 (m), 539 (m);

5: νMoO_4^{2-} : 943 (s), 719 (s); δMoO_4^{2-} : 542 (w), 524 (w), 510 (m);

6: νMoO_4^{2-} : 940 (m), 899 (m), 799 (vs); δMoO_4^{2-} : 692 (m), 659 (w);

7: νMoO_4^{2-} : 820 (s), 790 (vs), 760 (s); δMoO_4^{2-} : 680(s), 610 (s), 580 (m);

8: νMoO_4^{2-} : 953 (sh), 900 (vs), 790 (vs), 750 (vs); δMoO_4^{2-} : 621 (m), 500 (m);

9: νMoO_4^{2-} : 980 (sh), 965 (vs), 941 (vs), 860 (s), 780 (s), 754 (s), 748 (s); δMoO_4^{2-} : 650 (s), 630 (vs), 570 (s).

From these infrared data, we have suggested:

For **1** a discrete structure in which the molybdate anion behaves as a tetrachelating ligand, the environments around tin centres being octahedral as in [10] (Figure 1).

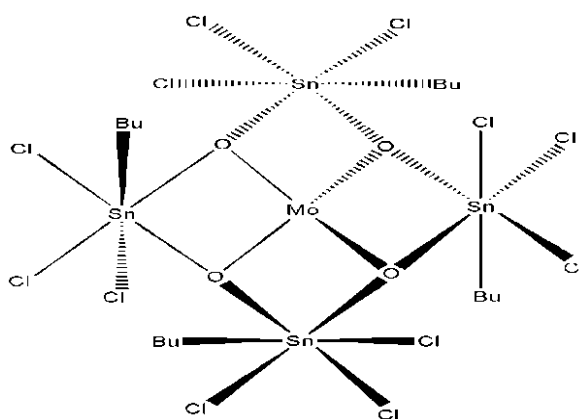


Figure 1. Proposed structure for compound **1**

For **2** a discrete structure with two molybdate anions monochelating the tin centre, the environment around the tin centre being octahedral (Figure 2).

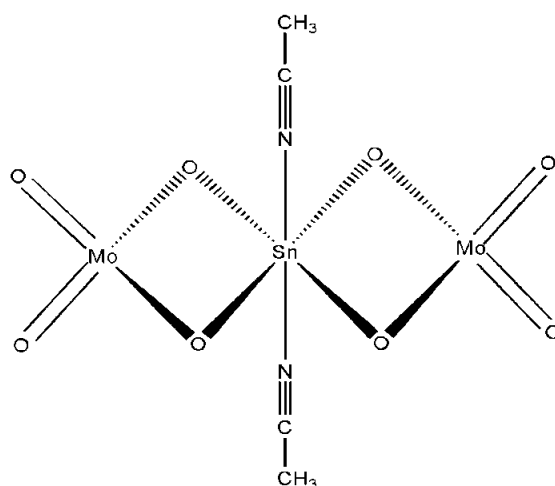


Figure 2. Proposed structure for compound 2

For **3** a discrete structure with a molybdate anion bichelating two SnCl_4 molecules leading to octahedral environments around tin centres (Figure 3).

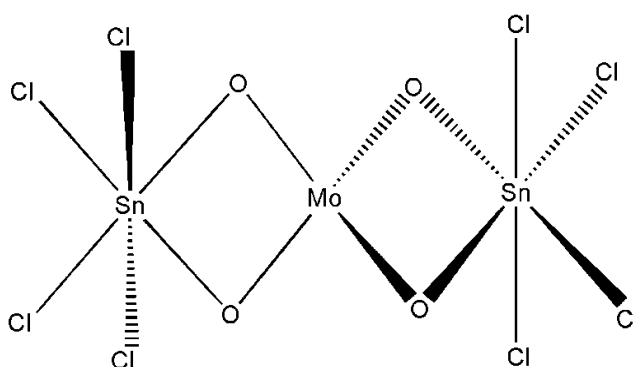


Figure 3. Proposed structure for compound 3

For **4** a discrete structure with bichelating and monochelating molybdate anions, the environment around the tin being octahedral (Figure 4).

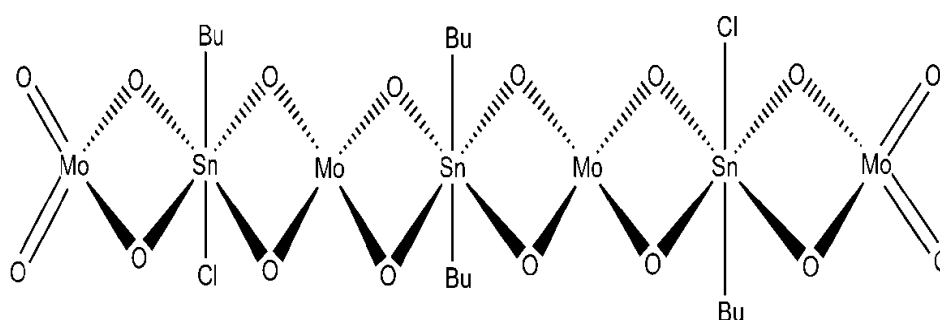


Figure 4. Proposed structure for compound 4

For **5** a discrete structure with a MoO_4 acting as a monochelating ligand, the water molecules being coordinated leading to an octahedral environment around the tin atom (Figure 5a).

A second dimeric structure is also possible with bridging bidentate anions (Figure 5b).

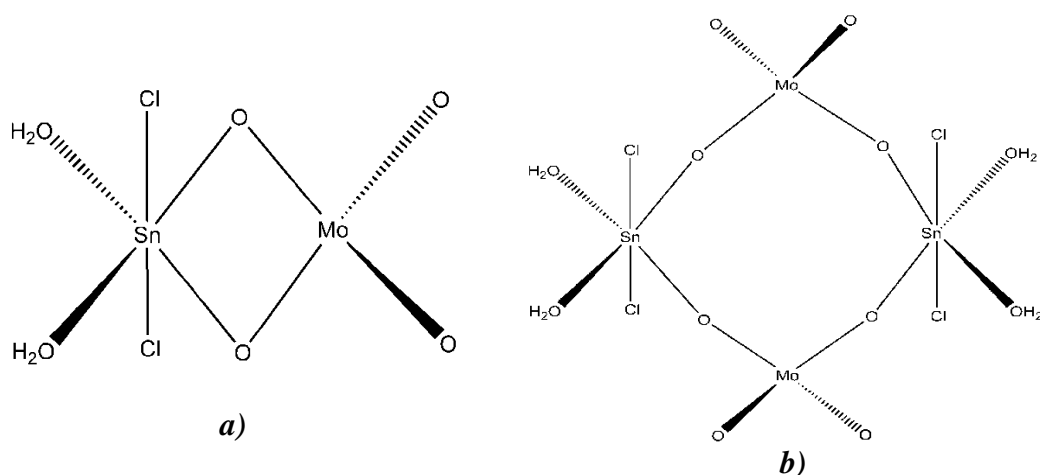


Figure 5. Proposed structures for compound 5

For **6** a discrete structure with a central bichelating anion (T_d symmetry) and two external monochelating ones, the environments around the tin centres being *trans* octahedral (Figure 6). This type of structure has yet been reported for $[(SnPh_2)_2(C_2O_4)_3]^{2-}$ [17].

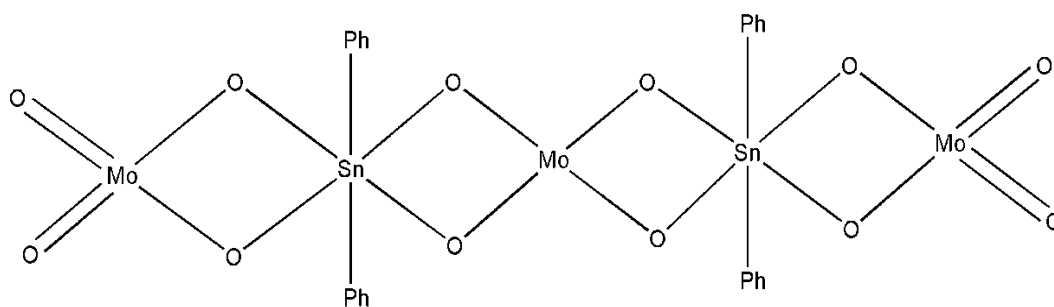


Figure 6. Proposed structure for compound 6

For **7** while considering the complex-anion $[(SnCl_4)_2(MoO_4)_3]^{6-}$ with internal bidentate and external monodentate tetrahedral molybdate anions coordinating the $SnCl_4$ molecules, we have suggested a dimer in which the complex-anions are linked by the cations through $O \cdots cation \cdots O$ hydrogen bonds, the environment around tin centres being octahedral (Figure 7a). We also have suggested an infinite chain structure of the dimer, the infinite chain being ensured by cations *via* $O \cdots cation \cdots O$ hydrogen bonds (Figure 7b).

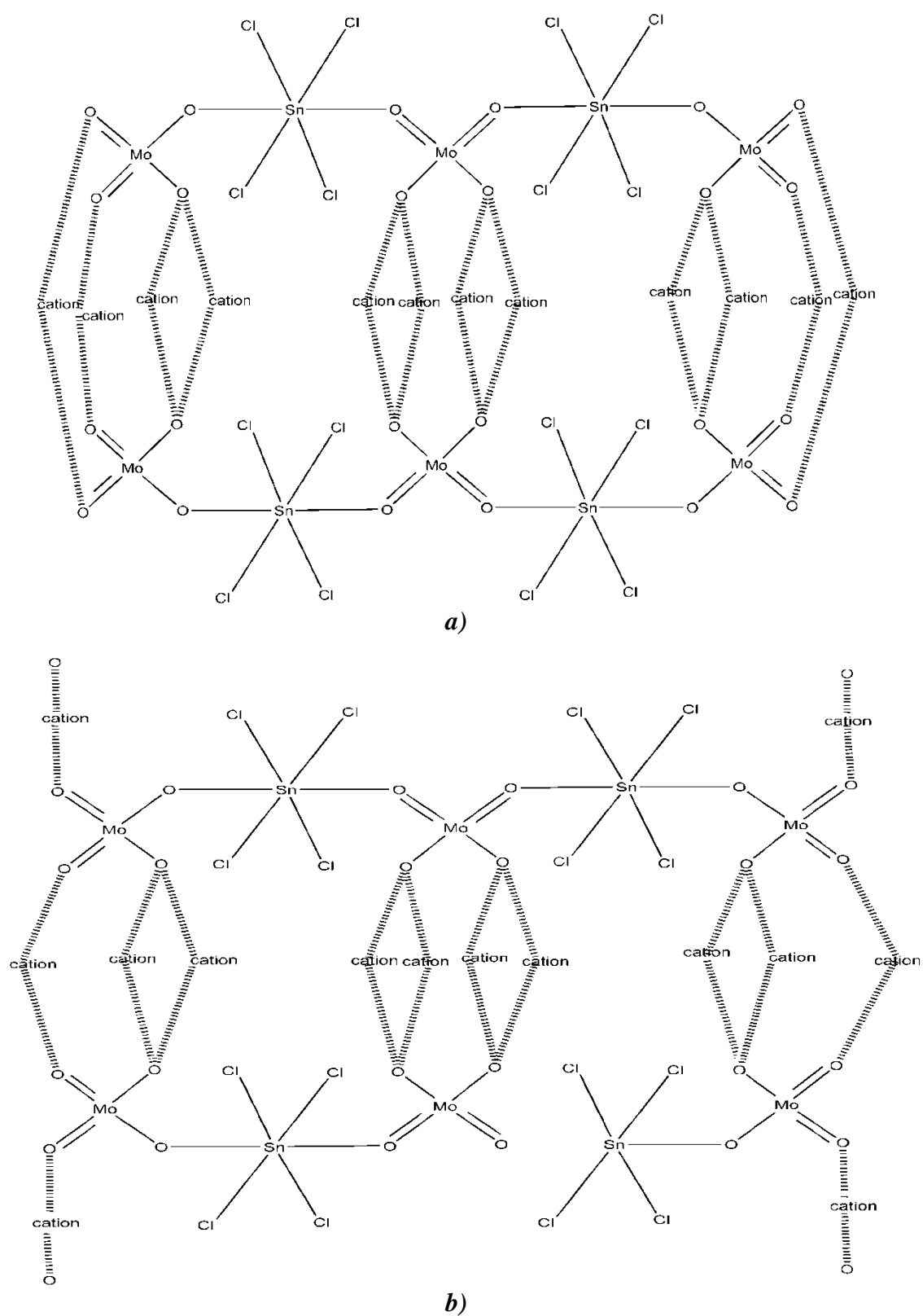


Figure 7. Proposed structures for compound 7

For **8** we suggest for the anion $[(\text{SnCl}_2\text{MoO}_4)_2.\text{Sn}(\text{MoO}_4)_3]^{2-}$ a discrete structure in which the central molybdate trichelates two $\text{SnCl}_2\text{MoO}_4$ and one $\text{Sn}(\text{MoO}_4)_2$ whereas the external ones are monochelating, the environments around the tin atoms being octahedral (Figure 8).

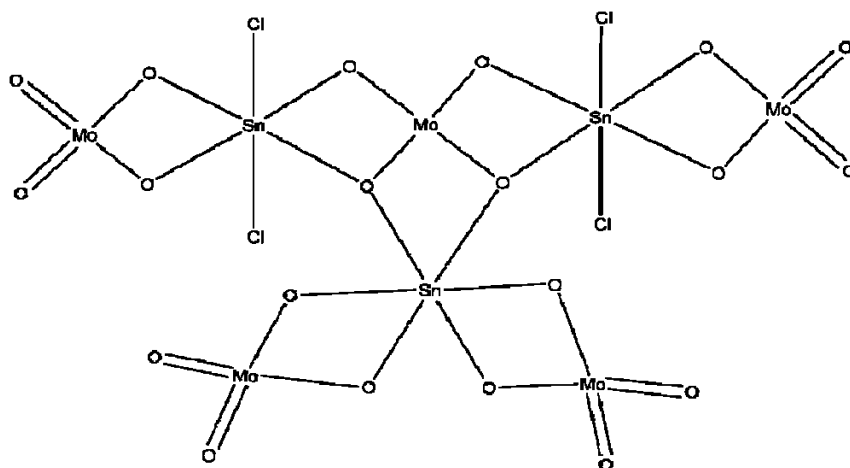


Figure 8. Proposed structure for compound **8**

The complex-anion $[\text{SnBuCl}_3.2\text{Sn}(\text{MoO}_4)_3]^{4-}$ contains two complex-anions $[\text{Sn}(\text{MoO}_4)_3]^{2-}$ which contain monochelating anions; we suggest for **9** a SnBuCl_3 molecule monocoordinated by the complex-anions, the environment being octahedral around the tin centres (Figure 9).

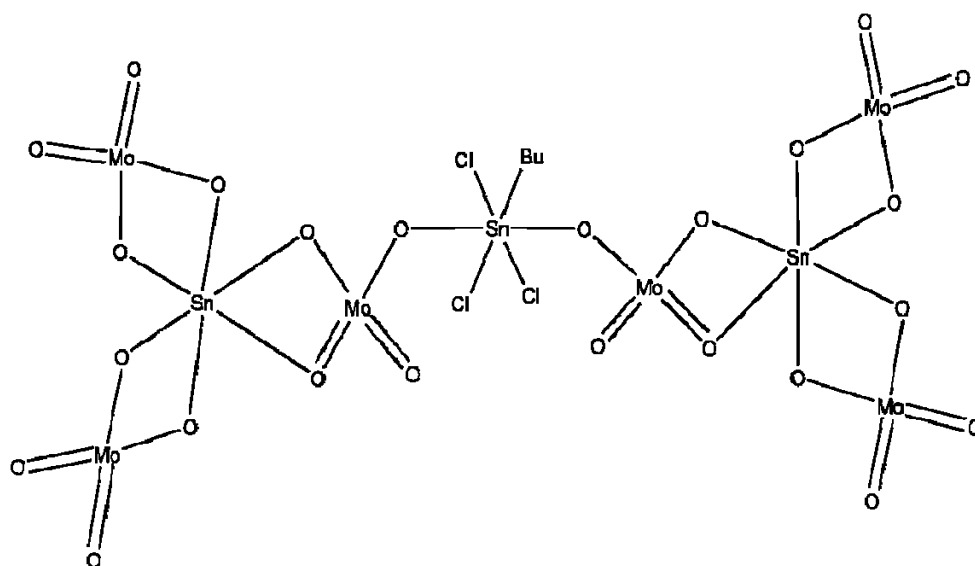


Figure 9. Proposed structure for **9**

In the proposed structures for **1**, **3**, **4**, **5**, **6**, **8** and **9** the cations or water molecules may interact through hydrogen bonds leading to supramolecular architectures.

CONCLUSION

The studied adducts and complexes have discrete or infinite chain structures, the molybdate behaving as a mono-, bi-, tetrachelating, a bidentate or a monochelating and monodentate ligand, the environment around the tin centres being octahedral. Supramolecular architectures may be obtained while considering extra hydrogen bonds involving the cations or water molecules in most of the studied compounds.

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