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Transition Metal-Assisted Hydrolysis of Pyrazole-Appended Organooxotin Carboxylates Accompanied by Ligand Transfer

Vadapalli Chandrasekhar,*[a] Pakkirisamy Thilagar,[a] and Tapas Senapati[a]

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The reaction of the potentially multi-site coordination ligands $[\{n\mathrm{Bu_2SnO_2CL}\}_2\mathrm{O}]_2$ (**1**), $[\{n\mathrm{Bu_2SnO_2CL'}\}_2\mathrm{O}]_2$ (**2**), $[n\mathrm{BuSn(O)O_2CL}]_6$ (**3**), and $[n\mathrm{BuSn(O)O_2CL'}]_6$ (**4**), (L = $\mathrm{(Pz)_2CH}$-); L′ = $\mathrm{(3,5\text{-}Me_2Pz)_2CH}$-; Pz = pyrazolyl) with hydrated metal salts leads to the hydrolysis of the organotin carboxylates accompanied by the formation of insoluble organotinoxide/hydroxides and metal complexes. The in situ generated LCOO and L′COO ligands bind to the metal ions. The complexes $[\mathrm{Cu(LCOO)_2(NO_3)_2}(n\mathrm{Bu_2Sn((H_2O)_2)})]_n[\mathrm{Cu(LCOO)_2}]$ (**5**), $[\mathrm{Mg(L'COO)_2}]$ (**6**), $[\mathrm{Cu(LCOO)_2}]$ (**7**), and $[\{(\mathrm{Cu(L'COO)_2}\text{-}(\mathrm{Cu(MeOH)})_3\}\{\mathrm{ClO_4}\}_2]_n$ (**8**) were isolated and structurally characterized. The solid-state structure of **5** reveals that two discrete molecules are present in the same asymmetric unit; a heterobimetallic coordination polymer, $[\mathrm{Cu(LCOO)_2(NO_3)_2}\text{-}(n\mathrm{Bu_2Sn((H_2O)_2)})]_n$ and a discrete coordination complex, $[\mathrm{Cu(LCOO)_2}]$. The cationic portion of the heterobimetallic compound contains alternate six-coordinate $\mathrm{Sn^{IV}}$ and $\mathrm{Cu^{II}}$ centers bridged by the carboxylate oxygen atoms of the LCOO ligand.

Introduction

Synthetic polymers in spite of their many attractive features[1–2] suffer from a serious disadvantage.[1–2] Even in well-controlled polymerization pathways the chain lengths as well as the molecular structure of the various individual chains present in a given macromolecule are not the same. *Dendrimers* or *Star-burst* molecules are hyperbranched macromolecules with high surface area and structural symmetry which retain the advantages of the macromolecules while avoiding the structural imprecision found in the latter.[3–5] We and others have been pursuing the possibility of using inorganic cores for building star-burst-type molecules.[6–14] Thus, inorganic rings such as cyclophosphazenes,[6,8] cyclosiloxanes,[9] and borazines[10] have been used recently as supports for the preparation of novel compounds which contain a central inorganic core and a periphery of judiciously placed functional substituents. Other inorganic rings and cages that contain Al–N or Al–C units have been similarly investigated.[11]

We have been interested in organostannoxanes for some time now and have recently shown the utility of these compounds to support hexa-ferrocene[12] and hexa-porphyrin[13] architectures. Encouraged by the success in the use of stannoxanes as inert cores for supporting a functional periphery we have turned our attention to the possibility of building multi-site coordination ligands based on stannoxane cores. Accordingly we have recently reported a series of multi-site coordination ligands containing a central stannoxane core which is decorated by a periphery of bis-pyrazolyl groups.[14] By a one-step synthetic protocol involving the reaction of bis(pyrazol-1-yl)acetic acid, LCOOH, (L = $\mathrm{(Pz)_2CH}$-) or bis(3,5-dimethylpyrazol-1-yl)acetic acid, L′COOH (L′ = $\mathrm{(3,5\text{-}Me_2Pz)_2CH}$-) with various organooxotin precursors potentially multi-site coordination ligands $[\{n\mathrm{Bu_2SnO_2CL}\}_2\mathrm{O}]_2$ (**1**), $[\{n\mathrm{Bu_2SnO_2CL'}\}_2\mathrm{O}]_2$ (**2**), $[n\mathrm{BuSn(O)O_2CL}]_6$ (**3**), and $[n\mathrm{BuSn(O)O_2CL'}]_6$ (**4**), were prepared.[14] The number of coordination units assembled on the stannoxane periphery depends on the type of stannoxane assembled. Metalation reactions of **1**–**4** with hydrated metal salts resulted, in all the cases, in the transfer of the bis(pyrazolyl)acetate unit from the tin to the transition/alkaline earth metal ion. In one instance involving the interaction between $[\{n\mathrm{Bu_2SnO_2CL}\}_2\mathrm{O}]_2$ (**1**) (L = $\mathrm{(Pz)_2CH}$-; Pz = pyrazolyl) and $\mathrm{Cu(NO_3)_2\cdot 3H_2O}$ we isolated $[\mathrm{Cu(LCOO)_2}\text{-}\mathrm{(NO_3)_2}(n\mathrm{Bu_2Sn(H_2O)_2})]_n$ $[\mathrm{Cu(LCOO)_2}]$ (**5**). The crystal structure of the latter reveals that its asymmetric unit contains two independent chemical entities viz., a heterobimetallic coordination polymer $[\{\mathrm{Cu(LCOO)_2}\}\{n\mathrm{Bu_2Sn}\text{-}\mathrm{(H_2O)_2}\}]_n$ (**5a**) and a discrete six-coordinate copper complex $[\mathrm{Cu(LCOO)_2}]$ **5b**. The structure of the heterobimetallic complex provides the clue that the transfer of the ligand from

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[a] Department of Chemistry, Indian Institute of Technology, Kanpur,
Kanpur 208016, India
Fax: +91-512-2590007, -2597436
E-mail: vc@iitk.ac.in

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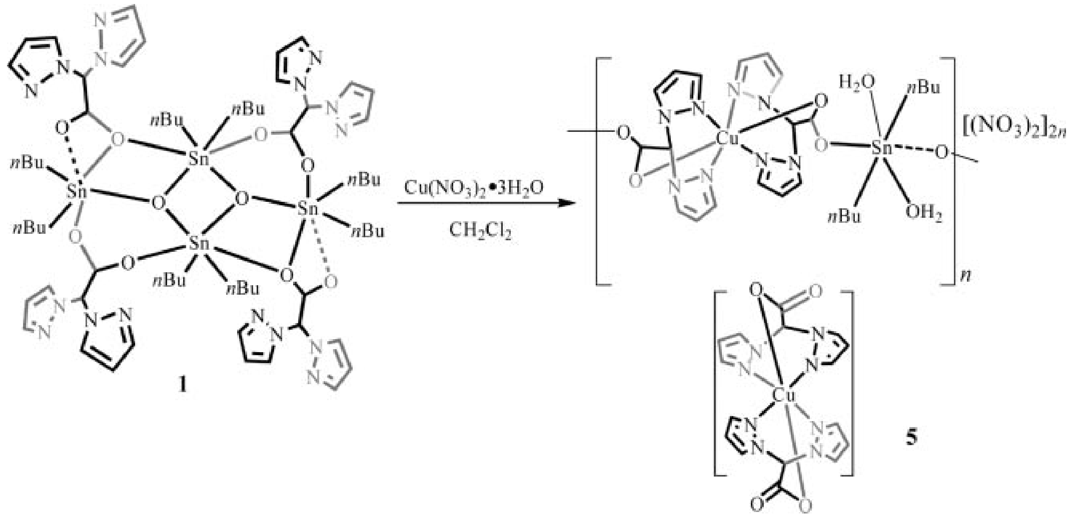
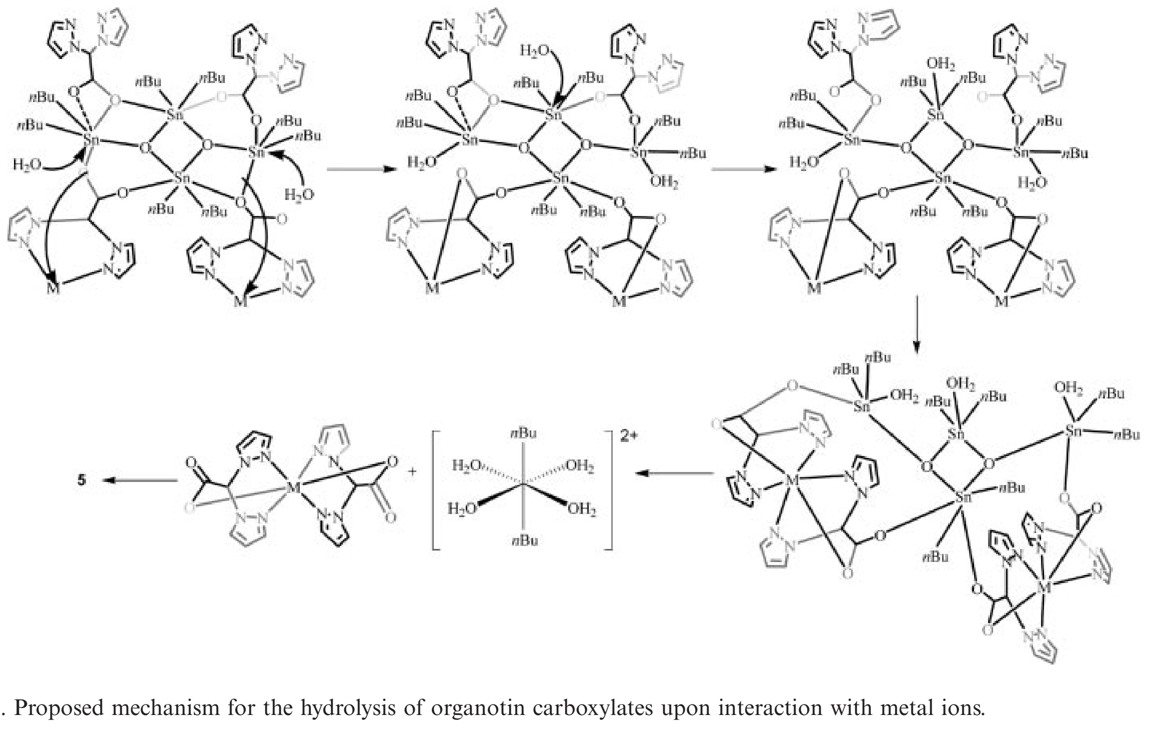
the organotin compound to the transition metal ion is probably initiated and accompanied by a hydrolysis reaction.

Results and Discussion

Synthesis: Compounds **5**–**8** were obtained in the reactions of the organotin precursors **1**–**4** with various hydrated metal salts (Scheme 1 and Supporting Information). In all these cases an insoluble colorless solid presumably a mixture of organotinoxide/hydroxides, was also isolated. For example, in the reaction of **3** with $Cu(ClO_4)_2{\cdot}6H_2O$ the insoluble material, **7b**, was obtained. The powder XRD of **7b** matches very closely that of *n*BuSn(O)OH based on its powder XRD (Figure S1, Supporting Information). Similarly the solid-state IR spectrum of **7b** also is in agreement with the spectrum of the authentic *n*BuSn(O)OH sample (Supporting Information, Figure S2). The insoluble product obtained in the reaction of metal salts with $Cu(NO_3)_2{\cdot}3H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ has a powder XRD pattern similar to that of $n\mathrm{Bu}_2\mathrm{SnO}$ (Supporting Information Figure S3–S4). These results imply that the organotin carboxylate cores of **1**–**4** decompose upon interaction with metal salts releasing hydrated organotin cations (Scheme 2) which can self-condense to afford organotin oxides/oxide hydroxides. In the process, the carboxylate ligand originally bound to the tin center is transferred to the interacting transition metal ion. Compound **5** is obtained in the reaction of **1** and Cu-



Scheme 1. Synthesis of **5**.



Scheme 2. Proposed mechanism for the hydrolysis of organotin carboxylates upon interaction with metal ions.

$(NO_3)_2\cdot 3H_2O$ (Scheme 1) and is probably an intermediate on the way to the fully hydrolyzed products. One of the molecules present in the crystal structure of **5a** is a heterobimetallic coordination polymer containing both tin and copper atoms (Figure 1). We were unable to obtain a ^{119}Sn NMR for this compound because of the strong paramagnetic relaxation of Cu^{II}.

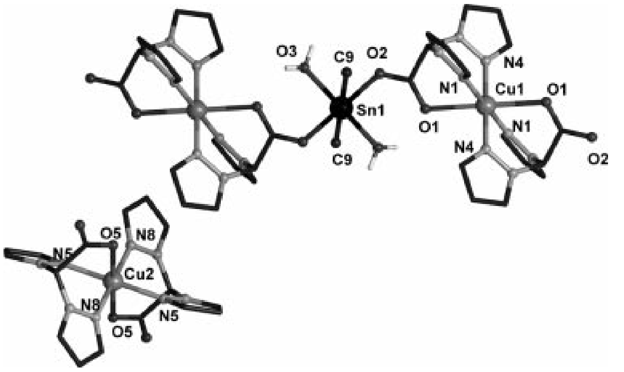


Figure 1. Independent crystallographic components of compound **5** with atom numbering. Heterobimetallic coordination polymer (top) and discrete mononuclear Cu^{II} complex (bottom). Only the alpha carbon of the *n*-butyl group is shown. The other carbon atoms of the butyl group and the hydrogen atoms of the pyrazolyl rings are removed for the sake of clarity.

X-ray Crystal Structure of 5

The X-ray structure of **5** is discussed herein. The structures of **6**–**8** along with their description and supramolecular structures are given in supporting information.

The crystal structure of **5** is quite unusual. Its asymmetric unit contains two independent chemical entities viz., a heterobimetallic coordination polymer $[\{Cu(LCOO)_2\}\{nBu_2Sn(H_2O)_2\}]_n$ (**5a**) and a discrete six-coordinate copper complex $[Cu(LCOO)_2]$ **5b**. However, these two chemical entities are intimately related as discussed vide infra.

Complex **5a** is a coordination polymer containing alternately two sub-units. One of these is $Cu(LCOO)_2$ while the other is $[nBu_2Sn(H_2O)_2]$. These are interlinked to each other to afford a one-dimensional helical polymer chain (Figure 1). Such a heterobimetallic coordination polymer is unprecedented among organotin compounds. The geometry around both of the metal ions found in **5a** can be described as distorted octahedral (Figure 2). The dihedral angle between the two square planes around Cu^{II} and Sn^{IV} is 16.322(5)°. The equatorial plane around Cu^{II} is formed by four pyrazole nitrogen atoms derived from two LCOO moieties. The apical positions are occupied by two carboxylate oxygen atoms (O1 and O1′). The two uncoordinated oxygen atoms (O2 and O2′) of the $[Cu(LCOO)_2]$ unit assist in forming the coordination polymer by bridging two $[nBu_2Sn(H_2O)_2]$ units (Figure 2). As a result the immediate coordination environment around Sn^{IV} consists of two *n*-butyl groups (C9 and C9′), two water molecules (in the equatorial plane) and two oxygen atoms (O2 and O2′) in the axial sites. The two *n*-butyl groups are arranged in a *trans* manner with respect to each other. In spite of two different oxygen donors the Sn–O bond lengths in **5a** are nearly similar (Sn1–O2, 2.219(1); Sn1–O3, 2.207(1) Å). In the case of the copper sub unit of **5a** the Cu1–O1 distance is 2.381(1) Å. Interestingly, all the metric parameters found for the copper subunit in **5a** are very similar to that found in **5b**. The formation of **5a** can be readily rationalized as follows. Hydrolysis of the organotin carboxylate **1** leads to the formation of $[nBu_2Sn(H_2O)_4]^{2+}$ and $Cu(LCOO)_2$. Interaction of these two entities results in the expulsion of two water molecules (that are *trans* to each other) from the former leading to the assembly of the heterobimetallic coordination polymer **5a** (Scheme 2). The presence of **5b**, fortuitously co-crystallizing with **5a**, strongly supports this supposition. Further, we have previously isolated $[nBu_2Sn(H_2O)_4]^{2+}$, albeit in a different reaction.[15]

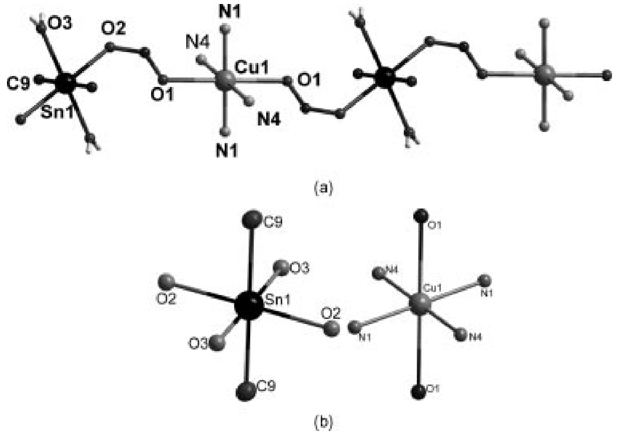


Figure 2. (a) Helical structure of compound **5** with atom numbering. The unlabeled atoms are generated by a symmetry relationship with the labeled atoms. (b) Coordination environment around Cu1 and Sn1. Important bond lengths [Å] and bond angles [°] in the monomer portion of the heterobimetallic polymer. Sn1–C9 2.133(2), Sn1–O3 2.207(1), Sn1–O2 2.219(1), Cu1–N4 1.995(1), Cu1–N1 2.013(1), Cu1–O1 2.381(1), C9–Sn1–C9 180, C9–Sn1–O3 86.137(7), O3–Sn1–O3 180, O2–Sn1–O2 180, N4–Cu1–N4 180, N4–Cu1–N1 91.355(6), N4–Cu1–O1 97.162(6), N1–Cu1–N1 180.0(6), N1–Cu1–O1 81.755(6), O1–Cu1–O1 180.

It must be mentioned that **1** itself does not undergo hydrolysis (Experimental Section). This means that the interaction of the metal ion with the coordination periphery of the organostannoxane ligand **1** accentuates the electrophilicity of the tin center and renders them susceptible to attack by water. Transfer of the bis(pyrazolylcarboxylate) ligand to the transition metal ion is also helped by the pincer-like coordination action of the released LCOO tripodal ligand resulting in the formation of two chelating five-membered rings arising from the coordination of the carboxylate oxygen atom to the metal center (Scheme 2).

Supramolecular Structure of 5: The crystal structures of **5**–**8** show rich supramolecular architectures mediated by intermolecular C-H---O, C-H---N, and O-H---O interactions. Only the case of **5** is discussed here. The remaining supramolecular structures are given in the Supporting Information (Figures S8–S12). The crystal structure of **5** shows interesting supramolecular interactions between **5a**

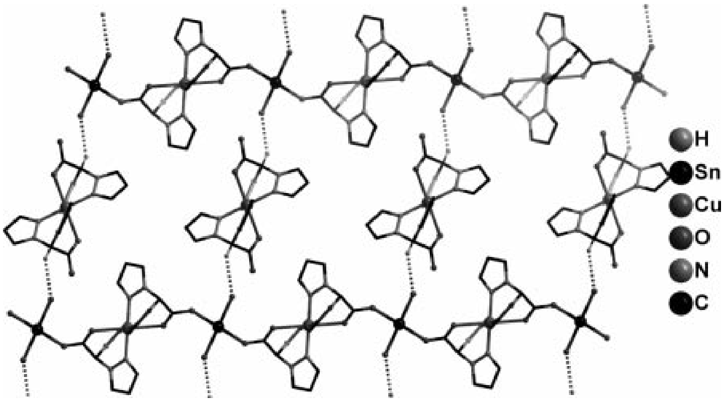


Figure 3. The 2D layer structure of compound **5** as a result of intermolecular C-H---O interactions [C19–H19···O13 2.673(1) Å and C19-H19---O13 134.747(11)°].

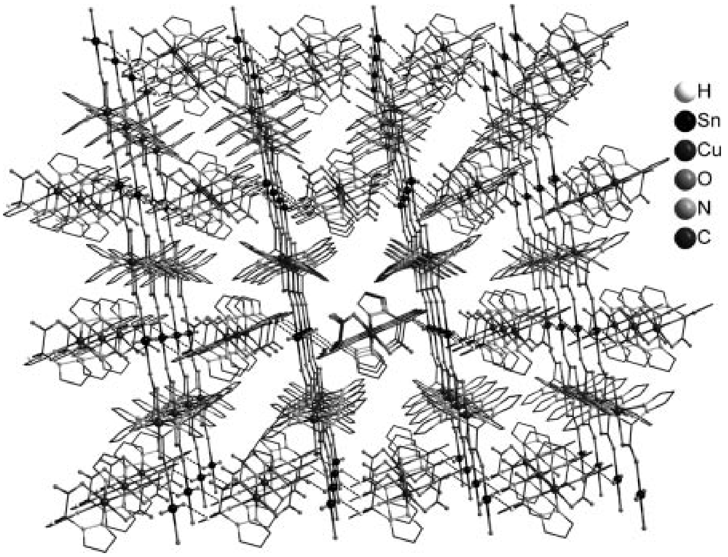


Figure 4. The 3D structure of **5**.

and **5b**. An intermolecular C-H---O interaction between the Pz_2-C-*H*-COO- of **5b** and an oxygen atom (belonging to a water molecule coordinated to tin) leads to the generation of a two-dimensional layer structure (Figure 3). Further intermolecular C-H---O interactions between the C-H′s of pyrazolyl ring of **5b** and the oxygen atoms of the nitrate anions leads to the elaboration of the supramolecular structure into a three-dimensional structure (Figure 4).

Conclusions

In conclusion, we report in this contribution, the hydrolytic sensitivity of the organostannoxane cages $[\{nBu_2SnO_2CL\}_2O]_2$ (**1**), $[\{nBu_2SnO_2CL'\}_2O]_2$ (**2**), $[nBuSn(O)O_2CL]_6$ (**3**), and $[nBuSn(O)O_2CL']_6$ (**4**), (L = $(Pz)_2CH$-); L′ = (3,5-$Me_2Pz)_2CH$-; Pz = pyrazolyl) upon interaction with hydrated metal salts. Interestingly, compounds **1**–**4** themselves do not hydrolyze in the absence of hydrated transition metal salts. This suggests that the coordination of the peripheral pyrazole arms of the organostannoxanes **1**–**4** renders the tin atoms electron deficient and therefore susceptible to nucleophilic attack by water leading to the collapse of the organostannoxane cores and the transfer of the ligands LCOO or L′COO to the metal ions. Another reason for the ligand transfer may be traced to the facile chelation that occurs *after* the ligand breaks off from the stannoxane and coordinates to the added metal ion. One of the ways of limiting this would be to insulate the tin atoms of the stannoxane core from the coordinating units by means of appropriate spacer groups. The delineation of this hypothesis is under progress.

Experimental Section

General: All solvents were dried and purified by standard procedures. $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, and $Mg(NO_3)_2{\cdot}6H_2O$ were purchased from Aldrich and used without further purification. Melting points were measured with a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out by using a Thermo-quest CE instruments model EA/110 CHNS-O elemental analyzer. IR spectra were recorded as KBr pellets with a Bruker Vector 22 FT IR spectrophotometer operating from 400 to

4000 cm^{-1}. Compounds **1**–**4** were synthesized according to procedures published by us recently.[14]

Synthesis of [Cu(LCOO)$_2$(NO$_3$)$_2$(*n*Bu$_2$Sn(H$_2$O)$_2$)]$_n$[Cu(LCOO)$_2$] (5): To a solution of **1** (0.2 mmol, 345 mg) in dichloromethane (100 mL) was added Cu(NO$_3$)$_2$·3H$_2$O (0.4 mmol, 93 mg). The reaction mixture was stirred for 2 h at room temperature. An insoluble white solid (**5′**) was removed by filtration. The white solid **5′** has a powder XRD pattern similar to [*n*Bu$_2$SnO$_2$]$_n$. The blue filtrate was concentrated to half of its volume and kept for crystallization. Blue crystals started to form after about a week. The crystals were collected, washed with diethyl ether, and dried. Total yield of the blue crystals: 34% (150 mg), m.p. 192–195 °C (d). IR (KBr): $\tilde{\nu}$ = 3341.0 (b), 3154.2–3124.7 (s, d), 2999.5 (w), 2959.2 (s), 2926.2 (s), 2863 (w), 1663.1 (s), 1515.1 (s) 1470.7 (s) 1410.4 (s), 1375.9 (s), 1291.6 (s), 1200.6 (w) 1102.2 (s), 1070.0 (w), 940.3 (w), 773.9 (s) and 749.9 (w) cm^{-1}.

A blank experiment was also performed to check if **1** underwent hydrolysis in the absence of the metal salt. Compound **1** (0.10 mmol, 0.18 g) was dissolved in methanol (35 mL), to this was added 2 mL of water. The reaction mixture was stirred for 3 h at room temperature. It was observed that **1** could be fully recovered. This was confirmed by the ^{119}Sn NMR [CDCl$_3$: δ = –172.1 (s), –195.5 (s) ppm] of **1** before and after performing the hydrolysis experiment.

Synthetic procedures for compounds **6**–**8**, IR and powder XRD traces for fully hydrolyzed products and their corresponding organooxotin precursors, molecular and supramolecular description for compounds **6**–**8** are given in the Supporting Information.

X-ray Crystallography: The crystal data for **5**–**8** were collected with a Bruker Smart diffractometer. All the structures were solved by direct methods using SHELXS-97[16] and refined by full-matrix least-squares on F^2 using SHELXL-97. All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. The asymmetric unit of compound **5** contains two independent structural entities. (1) A portion of a coordination polymeric chain with one copper (Cu1) and one tin (Sn1). (2) Half of the molecule of a mononuclear copper complex. All the metals in the asymmetric unit (Cu1, Sn1, and Cu2) have 0.5 occupancy. The asymmetric unit of compound **6** contains half of the molecule with two lattice water molecules (O3 and O4). The magnesium atom (Mg1) has 0.5 occupancy in the asymmetric unit and the oxygen atom (O4) of the lattice water molecule is disordered over two positions with 0.5 occupancies. The asymmetric unit of compound **7** contains half of the molecule with one copper center (Cu1) and the copper atom has 0.5 occupancy. The asymmetric unit of **8** contains two perchlorate molecules and a fraction of polymeric chain with three copper centers Cu1, Cu2, and Cu3. The atoms Cu1 and Cu3 have 0.5 occupancy in the asymmetric unit. Two of the perchlorate oxygen atoms (O11 and O14) are disordered. O11 is disordered over two positions with occupancies of 0.5 (O11a) and (O11b) and refined anisotropically. O14 is disordered over three positions with occupancies 0.4(O14a), 0.3 (O14b), and 0.3 (O14c), and are refined isotropically. Because of the inadequate quality of data we were unable to fix the hydrogen atoms on the oxygen atoms of the methanol molecules (O5, O6, and O7).

CCDC-608022, -608024, and -608027 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Figures 1–4 were obtained from the DIAMOND 3.0 software package.

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