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Cyclophosphazene-Organostannoxane Hybrid Motifs in Polymeric and Molecular Systems

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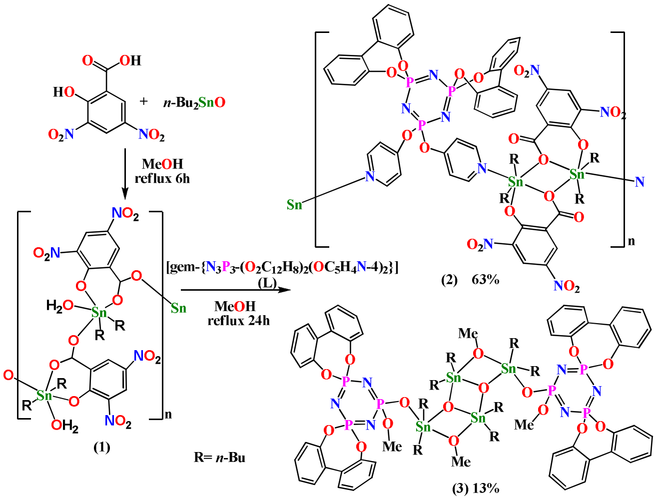
We report two hybrid inorganic ring systems in polymeric as well as monomeric forms. Both of these contain interconnected cyclophosphazene-stannoxane motifs.

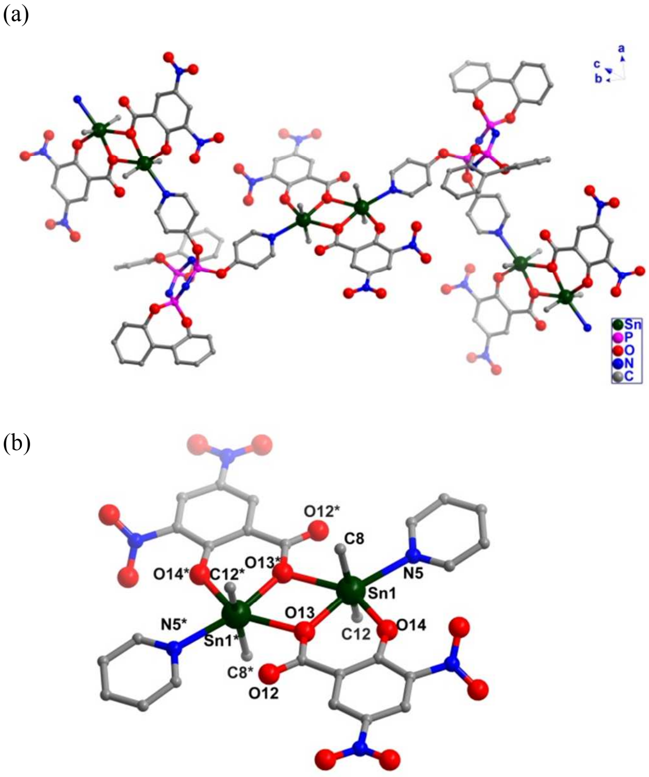
Cyclophosphazenes are an important family of inorganic heterocyclic ring systems with a well-developed chemistry at the small molecule level that has relevance to the corresponding high-polymers, viz., polyphosphazenes.[1] In recent years there have been efforts to utilize cyclophosphazenes and related families of inorganic heterocyclic compounds as scaffolds to build multi-site coordination ligands and utilize the latter to build polynuclear compounds.[2] Similarly, these ring systems have also been used as supports for the preparation of dendrimer-like compounds possessing functionalities that are electrochemically, photochemically or catalytically active.[3] Another prominent family of inorganic rings and cages consists of organostannoxanes which have attracted considerable interest in view of their enormous structural diversity as well as their utility as scaffolds for the construction of functional molecules.[4] Recently there have been efforts to build coordination polymers containing organotin nodes, some of these being useful for selective adsorption of gases.[5] In this contribution, we describe our efforts that have successfully culminated in the generation of novel hybrid ring systems containing *both* the cyclophosphazene and the stannoxane motifs in a single chemical structure. Accordingly, herein, we report the synthesis and structural characterization of $[gem\{N_3P_3(O_2C_{12}H_8)_2(OC_5H_4N\text{-}4)_2\}\{n\text{-}Bu_2Sn\text{-}OOCR(O)\}_2]_n$ (**2**) where R(OH)(COOH) = $[3,5\text{-}(NO_2)_2C_6H_2(OH)(COOH)]$ and $[gem\{N_3P_3\text{-}(O_2C_{12}H_8)_2\}(O)(n\text{-}Bu_2Sn)_2(\mu_3\text{-}O)(\mu\text{-}OMe)]_2.MeOH$ (**3**). While the former is a one-dimensional coordination polymer the latter is a molecular compound.

We have shown recently that pyridyloxycyclophosphazenes and –carbophosphazenes are excellent ligands for the preparation of molecular compounds as well as coordination polymers.[6] In view of this we were interested if we can build coordination polymers by the use of these ligands in combination with organostannoxanes. First, utilizing a known procedure, involving the reaction of $[n\text{-}Bu_2SnO]_n$ and R(OH)(COOH) a one-dimensional coordination polymer, $[n\text{-}Bu_2SnOOCR(O)H_2O]_n$[7] (**1**) was isolated (ESI, Figure S1). The reaction of **1** with *gem*-$N_3P_3(O_2C_{12}H_8)_2(OC_5H_4N\text{-}4)_2$ was carried out with a view to assemble a two-dimensional coordination polymer (ESI, Figure S2). Surprisingly, a slightly more complex reaction ensued affording the one-dimensional coordination polymer **2** (Scheme 1).

Scheme 1. Synthesis of compounds **2** and **3**



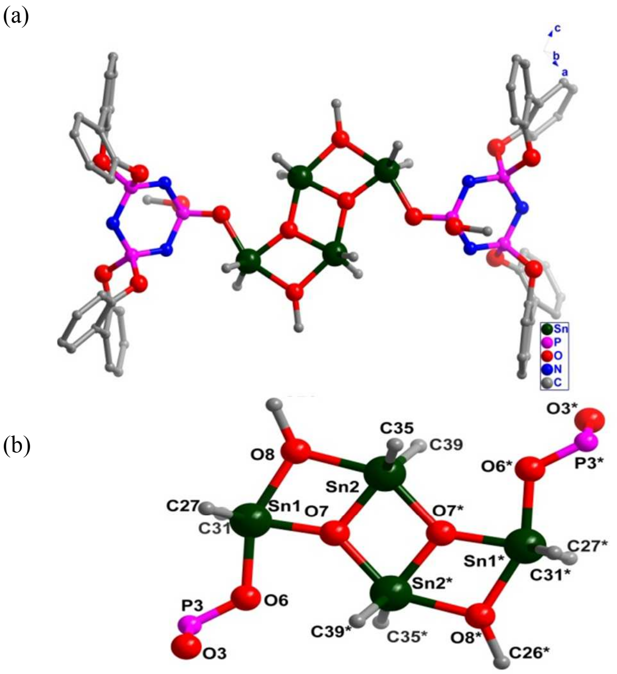
In this reaction the original coordination polymer **1** appears to break down into a monomer which dimerizes and reacts with the cyclophosphophazene ligand affording **2** (ESI, Scheme S1). The structure of **2** reveals a novel hybrid motif containing interlinked $\{Sn_2O_2\}$ and cyclophosphazene units. The distannoxane unit is assembled as a result of the bridging coordination action of the carboxylate ligand [Figures 1(a) and 1(b)]. The chelating coordination of the 3, 5-dinitrosalicylate ligand results in three contiguous rings (6-membered, 4-membered and 6-membered). Interestingly, all of these rings lie nearly in one plane (ESI, Figure S3). Although organostannoxanes are replete with distannoxane motifs, usually the bridging ligands are either hydroxide[7] or oxide [8] (in some instances alkoxides[9]). The current motif is similar to that found earlier in $[n\text{-}Bu_2Sn(C_{14}H_{10}N_2O_4)N]_2$,[10] $[(PhCH_2)_2Sn(C_{14}H_{10}N_2O_4)N]_2$[10] and $[Me_2Sn(OC_{10}H_6CH{=}NCH_2CH_2COO)]_2$[11] (ESI, Chart 1). Each cyclophosphazene ligand containing two well-directed coordinating arms (in the form of pyridyloxy groups) connect successive distannoxanes affording the zig-zag coordination polymer **2** (Figure 1 and ESI, Figure S4). The phosphazene ring in **2** is essentially planar. The $^{31}P\{^1H\}$ NMR spectrum of **2** along with the chemical shift and coupling constant parameters [δ ppm = 25.22 (d, $P(O_2C_{12}H_8)$), 9.59 (t, $P(O\text{-}C_5H_4N\text{-}3)_2$, $\{^2J(P–N–P)$ = 95.52 Hz}] is very similar to that observed for the parent cyclophosphazene ligand (ESI, Figure S5). The $^{119}Sn\{^1H\}$ NMR of **2** shows a singlet δ = -347 ppm which may be compared with that found in $[n\text{-}Bu_2Sn(C_{14}H_{10}N_2O_4)N]_2$[10] and $[(PhCH_2)_2Sn(C_{14}H_{10}N_2O_4)N]_2$[11] which have similar structural motifs (ESI, Figure S6).


(a)

(b)

Figure 1.(a) Cyclophosphazene pendant 1D-coordination polymer on organostannoxane backbone(b) Core of the polymer **2**. Selected bond parameters: Bond length (Å): Sn(1)-O(13), 2.194(28); Sn(1)-O(13)*, 2.426 9(35); Sn(1)-O(14), 2.131(39); Sn(1)-C(8), 2.127 (41); Sn(1)-C(12), 2.128(47); Sn(1)-N(5), 2.428 (35); Sn(1)-O(12), 2.911(39); Sn(1)-Sn(1)*, 3.894 (9). Angles (°): Sn(1)-O(13)-Sn(1)*, 114.80 (1); O(13)-Sn(1)-O(13)*, 65.19(1).

Although the coordination polymer **2** was the major product in the reaction of **1** and *gem*-$N_3P_3(O_2C_{12}H_8)_2(OC_5H_4N\text{-}4)_2$ (**L**), we were also able to isolate, during crystallization, minor quantities (~13%) of [*gem*-$\{N_3P_3(O_2C_{12}H_8)_2\}(O)(n\text{-}Bu_2Sn)_2(\mu_3\text{-}O)(\mu\text{-}OMe)]_2$.MeOH (**3**) (see ESI). In contrast to **2**, **3** is a molecular compound. Interestingly, **3** is formed as result of a P-O bond hydrolysis involving the pyridyloxy arms affording, in situ, the mono anionic ligand [*gem*-$N_3P_3(O_2C_{12}H_8)(OMe)(O)]^-$. P-O bond hydrolysis in pyridyloxycylcophosphazenes is not common and previously we reported a Co(II)-mediated hydrolysis reaction (ESI, Figure S7).[13] However, this is the first example of an organotin carboxylate-mediated P-O bond hydrolysis reaction. The molecular structure of **3** reveals a central tetrastannoxane motif that is present in a ladder-type structure. The termini of the ladder are connected to the cyclophosphazenes through the P-O-Sn bonds generating a novel cyclophosphazene-tetrastannoxane-cyclophosphazene hybrid. The metric parameters of **3** [Figures 2(a) and 2(b)] are comparable to those observed in compounds containing similar structural motifs.[14]The poor solubility of **3**, precluded its characterization in the solution.


(a)

(b)

Figure 2. (a) Molecular structure of **3**.(b) Core of compound **3**. Selected bond parameters: Bond length (Å): Sn(1)-O(6), 2.157(10); Sn(1)-O(7),1.996(11); Sn(1)-O(8), 2.211(11); Sn(1)-C(27), 2.09(2); Sn(1)-C(31), 2.14(2); Sn(2)-O(7), 2.044(10); Sn(2)-O(8), 2.183(12); Sn(2)-C(35), 2.08(3); Sn(2)-C(39), 2.12(2); Sn(2)-O(7)*, 2.138(11); P(4)-O(6), 1.517(12); P(4)-O(3), 1.572(11). Angles (°): O(6)-Sn(1)-O(7), 82.7(4); O(6)-Sn(1)-O(8), 154.4(4); O(7)-Sn(1)-O(8), 71.8(4); O(7)-Sn(2)-O(7)*, 73.8(5); O(7)-Sn(2)-O(8), 71.5(4); O(7)*-Sn(2)-O(8), 145.3(4); Sn(1)-O(7)-Sn(2), 115.0(5); Sn(1)-O(7)-Sn(2)*, 138.7(5); Sn(2)-O(7)-Sn(2)*, 106.2(5), Sn(1)-O(6)-P(3), 123.26(4); O(6)-P(3)-O(3), 102.47 (4).

In summary, we report two novel hybrid inorganic ring systems that contain interconnected cyclophosphazene-stannoxane motifs both in polymeric and molecular forms.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Crystallographic information files (CIF) for compounds**2-3** **(**CCDC 971483–971484),Experimental section and some additionalfigures for compounds**2-3**]. See DOI: 10.1039/b000000x/

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Graphical Abstract

Cyclophosphazene-Organostannoxane Hybrid Motifs in Polymeric and Molecular Systems

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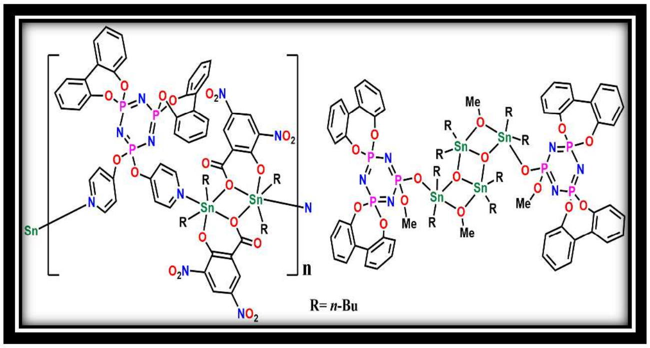

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The synthesis and structural characterization of two hybrid inorganic ring systems that contain interconnected cyclophosphazene-stannoxanemotifs are reported.