

Stannoxanes and phosphonates: New approaches in organometallic and transition metal assemblies

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Abstract. Phosphonate ligands, $[\text{RPO}_3]^{2-}$, are extremely versatile in the assembly of multi-tin and multi-copper architectures. We have used organostannoxane cores for supporting multi-ferrocene and multi-porphyrin peripheries. The copper-metallated multi-porphyrin compound is an excellent reagent for facile cleavage of DNA, even in the absence of a co-oxidant. Reaction of *t*-BuPO₃H₂ with Cu(ClO₄)₂·6H₂O in the presence of 2-pyridylpyrazole (2-Pypz) leads to the synthesis of a decanuclear copper (II) assembly.

Keywords. Organostannoxanes; organotin; multi-ferrocene; multi-porphyrin; phosphonates; pyrazoles.

1. Introduction

Organostannoxanes has been attracting considerable attention in recent years.^{1–4} This is due to several factors. One, the nature of the organotin oxide/hydroxide itself has been a matter of considerable interest. Depending on the 'R' group, the nature of the organotin oxide varies considerably (scheme 1).⁴

Two, the reactions of organotin oxides in general and that of *n*-butylstannonic acid, *n*-BuSn(O)OH, in particular with protic acids such as carboxylic, phosphonic, phosphinic or sulphonic acids has led to a wide range of structurally diverse products (scheme 2).^{1–4}

This article summarizes some of our recent research efforts in this area. We also show how the phosphonate ligand can be used for the preparation of multi-metal assemblies, particularly in conjunction with an ancillary ligand.

2. New structural forms in organotin clusters

The reaction of *n*-BuSn(O)OH with various types of protic acids leads to the formation of diverse types of products. These include *cube*, *drum*, *O-capped cluster*, *foot-ball cage*, etc. (scheme 2). In order to check whether by the use of two different types of reagents we can access new clusters, we investigated the reaction of *n*-BuSn(O)OH with H₃PO₃ in the

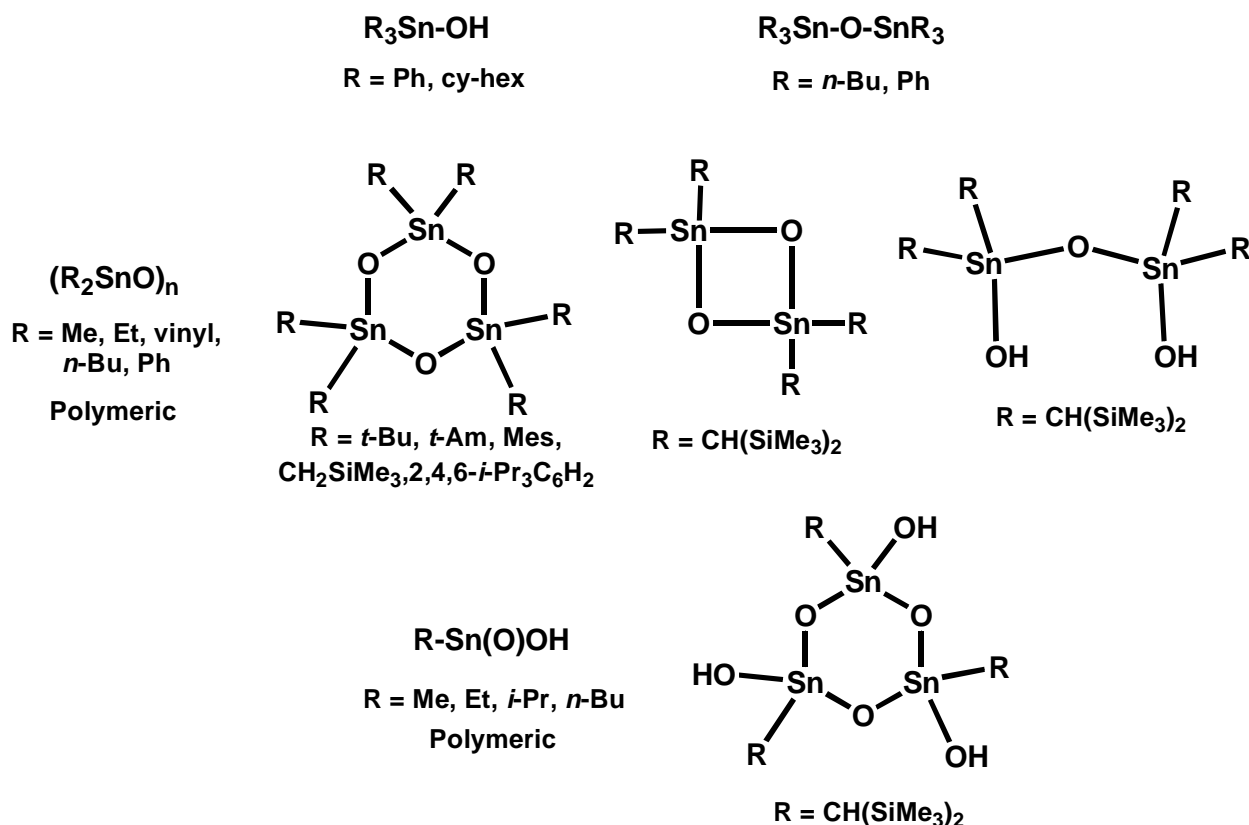
presence of phenols.^{3,5,6} We have observed the formation of new hexameric organostannoxane clusters, $\{[(n\text{-BuSn})_3(p\text{-X-C}_6\text{H}_4\text{-O})_3\text{O}]_2(\text{O}_3\text{PH})_4\}$, where X = H (**1**); Cl; Br and I (scheme 3).

These clusters contain two tri-tin motifs (two poles), viz., $[(n\text{-BuSn})_3(p\text{-X-C}_6\text{H}_4\text{-O})_3\text{O}]$, which are linked to each other by tridentate $[\text{HPO}_3]^{2-}$ ligands. Each of the tri-tin poles is held in place by a bridging ($\mu_3\text{-O}$) oxide ligand. The entire equator of the cage is spanned by four phosphonate ligands. It is interesting to note that the molecular structure of **1** is closely related to the *foot-ball cage*.^{7–10} The *foot-ball cage* also consists of two tri-tin poles; however, the equator of the molecule is made up of a $[(\text{RSn})_6\text{O}_{12}]$ unit.⁵ Further, the tri-tin pole structural motif of **1** as well as the *foot-ball cage* can be independently synthesized in a reaction involving *n*-BuSn(O)OH and Ph₂PO₂H/4-CH₃-C₆H₄SO₃H (scheme 2).^{8–10}

In contrast to the above reaction, where H₃PO₃ provides the tridentate coordination, we have investigated the reaction of 9-hydroxy-9-fluorene carboxylic acid (**LH**₂) with *n*-BuSn(O)OH in the presence of phenols (scheme 4).¹¹ In this case the carboxylic acid **LH**₂ provides the coordination environment through the carboxylate and the geminal C–OH oxygen atoms.

In this reaction, phenol does not react with *n*-BuSn(O)OH; it gets incorporated in the cage structure formed. The product $\{[n\text{-BuSn}(\text{OH})\text{L}]_6 \cdot 6\text{H}_2\text{O} \cdot 6\text{ROH} \cdot \text{CHCl}_3\}$ (**2**) is a hexameric organotin cage which contains three discrete Sn₂(OH)₂ units. These are stitched together by six tridentate dianionic ligands

*For correspondence



Scheme 1. Organotin oxides and hydroxides.

(L). The carboxylate group bridges two adjacent centres (scheme 5; A).

The arrangement of the six tin atoms in the molecular structure of **2** leads to a prismane type of arrangement where the short edges of the prism are bridged by μ -OH ligands (scheme 5; B). Compound **2** organizes itself in a supramolecular structure through several cumulative hydrogen-bonding interactions that occur between the organooxotin cage and guest phenol and water molecules. This leads to a columnar network which encapsulates alternately phenol/water and chloroform molecules in alternating hydrophobic and hydrophilic channels.¹¹

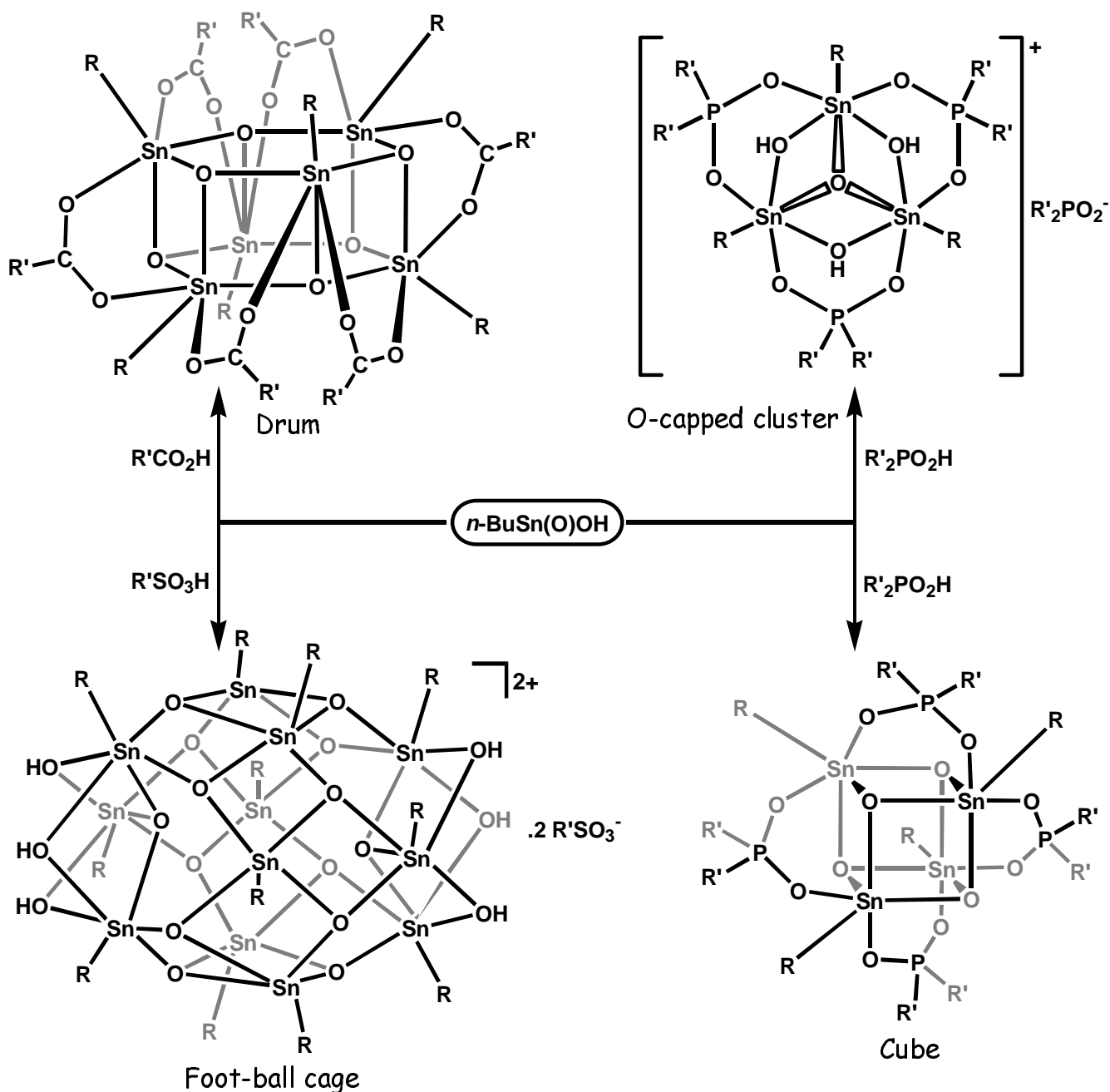
3. Organostannoxanes as supports for multi-ferrocene and multi-porphyrin assemblies

Although the reaction of organotin oxides/hydroxides with protic acids leads to various products, the current understanding of these reactions allows a predictable assembly. It was of interest to us to ascertain whether by choosing a specific reaction type we can generate a constant central stannoxane core

and vary its periphery. This strategy would allow the preparation of stannoxanes decorated with varying functionalities. To test this idea we reacted *n*-BuSn(O)OH with ferrocene carboxylic acid (FcCO₂H, Fc = ferrocenyl) in 6 : 6 ratio to afford quantitatively a hexa-ferrocene assembly, [*n*-BuSn(O)OCFc]₆ (**3**) in quantitative yields (scheme 6).¹²

The hexa-ferrocene assembly **3** contains a central Sn₆O₆ core (*drum*) and is surrounded by six ferrocene carboxylates. Each ferrocene carboxylate binds in a bidentate manner and bridges two adjacent tin centres. Remarkably, the hexa-ferrocene derivative **3** is quite stable, both thermally as well as electrochemically. All the six ferrocenes are equivalent and are oxidized at the same potential (+0.72 V vs SCE) (figure 1).

Further, even after ten electrochemical cycles the hexa-ferrocene derivative **3** does not decompose in solution. In order to understand if a modulation of the number of ferrocene units is possible, we have changed the organotin oxide starting material. Accordingly, the reaction of *n*-Bu₂SnO with FcCO₂H in 4 : 4 ratio affords a tetra-ferrocene derivative,



Scheme 2. Monoorganooxotin clusters.

$\{[n\text{-Bu}_2\text{SnOC(O)Fc}]_2\text{O}\}_2$ (**4**)¹³ (scheme 7) in a ladder type of a structure containing a central Sn_2O_2 ring and two terminal $\text{Sn}_2\text{O}_3\text{C}$ rings. On the other hand, reaction of Ph_2SnO with FcCO_2H in 1 : 1 and 1 : 2 molar ratio leads to the formation of a dinuclear assembly, $\{\text{Ph}_2\text{Sn}[\text{OC(O)Fc}]_2\}_2$ (**5**)¹³ that supports four ferrocene units (scheme 7).

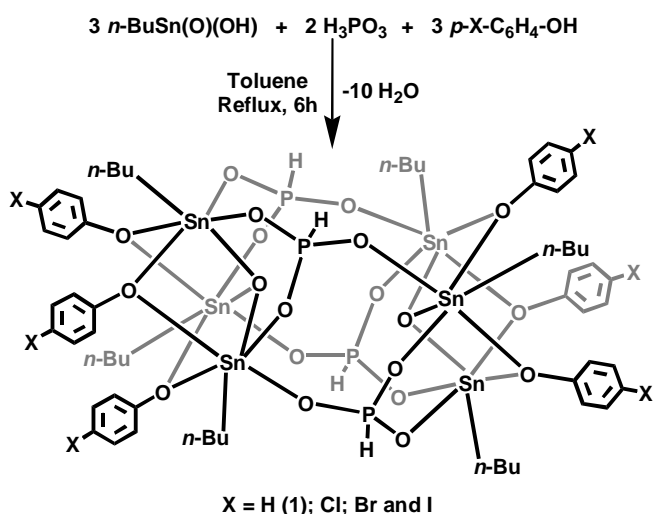
Molecular structure of the cluster **5** reveals that the ferrocene carboxylates are involved in both chelating and bridging coordination modes to the tin cen-

tres. This results in a central eight-membered ring (2Sn, 4O, 2C) and two terminal four-membered rings (1Sn, 2O, 1C). The cyclic voltammetry of $\{[n\text{-Bu}_2\text{SnOC(O)Fc}]_2\text{O}\}_2$ (**4**) reveals that it does not decompose under the electrochemical conditions and shows a single oxidation potential of +0.73 V (vs SCE).

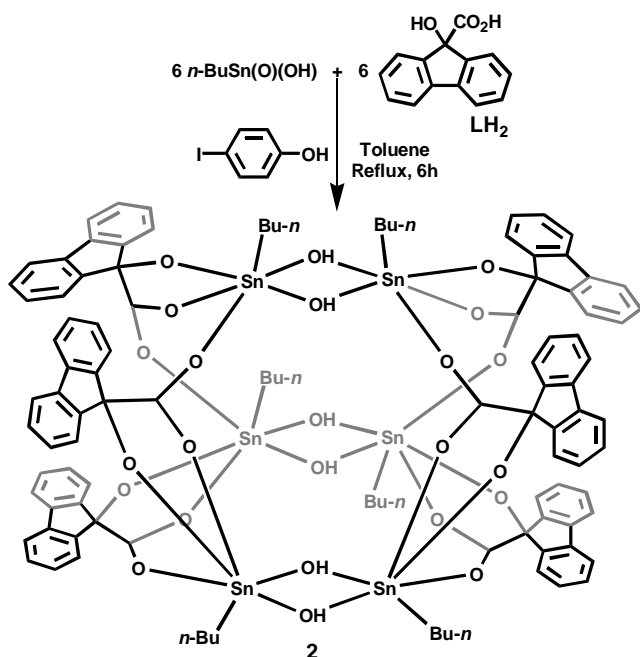
Spurred by the success of the synthesis of the multi-ferrocene assemblies, we extended this approach to the preparation of multi-porphyrin compounds.

Some of the important concerns in the multiporphyrin synthesis include solubility and yields of the final product. We reasoned that our methodology should afford multiporphyrin assemblies where each porphyrin would retain its independent "porphyrinic" character. Accordingly, the reaction of $H_2TTPCOOH$ with $n\text{-BuSn(O)OH}$ afforded a free-base *drum*, $[n\text{-BuSn(O)OC(O)TTPH}_2]_6$ (**6**) (scheme 8).¹⁴

The latter resonates at -482.4 ppm in its ^{119}Sn NMR indicating the formation of the hexameric *drum*. The free-base *drum* (**6**) was characterized by



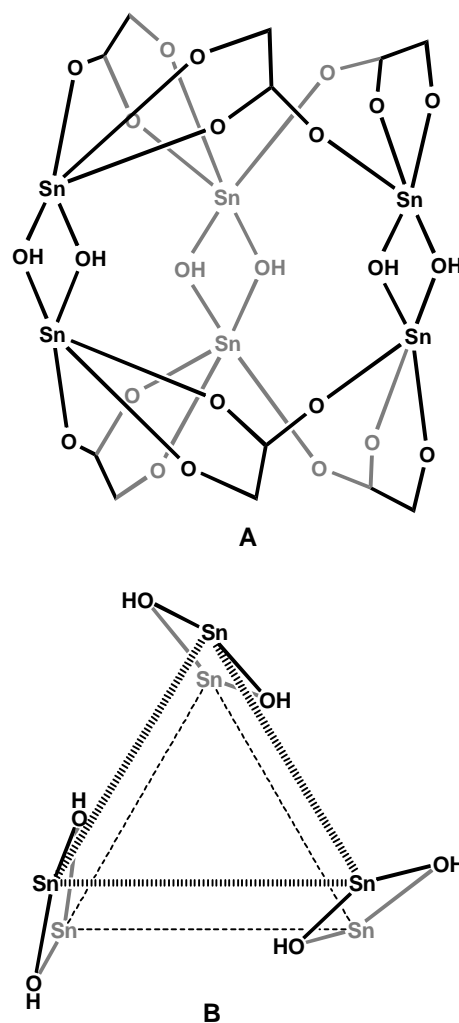
Scheme 3. Synthesis of double O-capped clusters.



Scheme 4. Synthesis of hexanuclear prismane cage **2**.

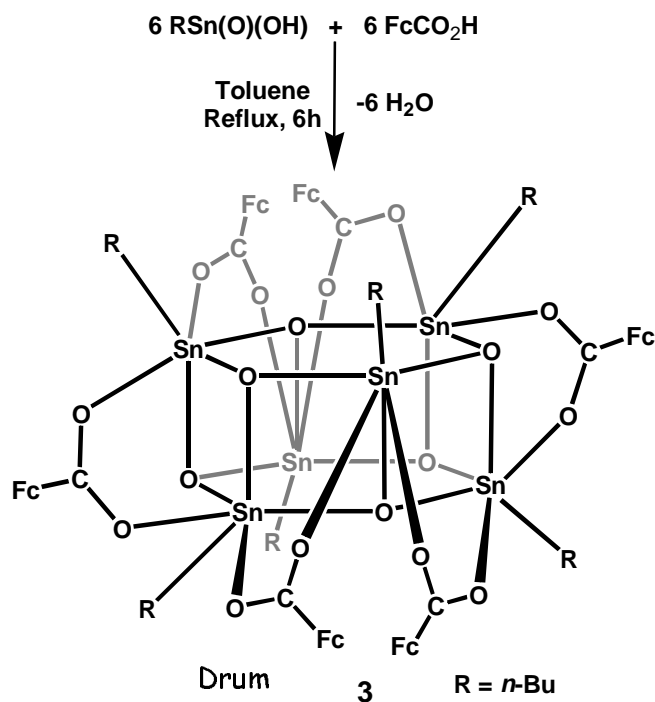
several methods including optical spectroscopy. Thus, it shows the characteristic Q- and S-bands in its UV-Vis spectrum. The free-base *drum* can be readily metalated without any decomposition of the stannoxane core. Metalation by Cu(II) is accompanied by the usual changes in the UV-Vis spectrum, viz., a reduction of the number of the peaks and the shift of the absorption maxima (figure 2). Further the axial symmetry of the Cu(II) ion in this assembly is readily inferred from its EPR spectrum ($g_{\parallel} = 2.1888$; $g_{\perp} = 2.0219$) (figure 3). It is also possible to obtain the hexa-metalated porphyrin *drum* by an alternative synthetic strategy. This involves a prior metalation of the porphyrin carboxylic acid followed by reaction with $n\text{-BuSn(O)OH}$ (scheme 8).

The Cu_6 -porphyrin *drum* (**7**) is an extremely effective reagent for rapid DNA cleavage even in the



Scheme 5. View of the inner core of the cage **2**.

absence of any co-oxidant.¹⁴ Interestingly, the free-base *drum* (**6**) itself is completely ineffective. Mechanistic studies have revealed that the DNA cleavage action of the Cu₆-porphyrin *drum* involves a possible role for superoxide anion radicals and H₂O₂. Further, this compound is completely inactive towards proteins such as lysozymes. Thus, **7** can potentially be used for selective removal of nucleic acid contaminants from cell extracts.



Scheme 6. Synthesis of hexa-ferrocene assembly **3**.

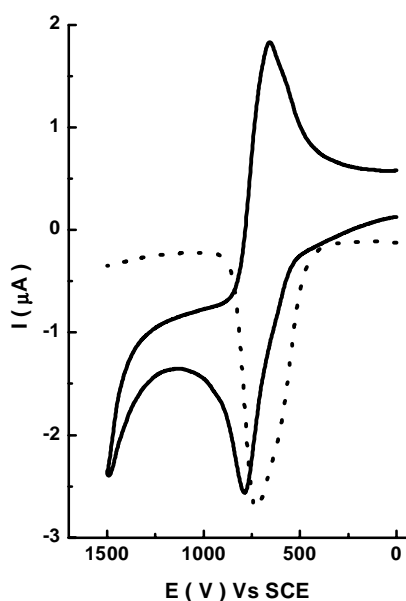


Figure 1. Cyclic voltammogram of **3**.

4. Phosphonate ligands for multi-metal assembly

We have shown above the utility of phosphonate ligands for the formation of multi-tin assemblies. We have also found that the reaction of appropriate transition metal precursors such as metal halides and metal perchlorates with *t*-butylphosphonic acid (in the presence of ancillary pyrazole ligands) leads to the formation multi-metal architectures. Previously we have observed the formation of dodecanuclear copper (Cu₁₂),¹⁵ trinuclear and hexanuclear zinc clusters¹⁶ in the reaction of the appropriate metal salts with *t*-butylphosphonic acid and 3,5-dimethylpyrazole. Recently, we have found that the reaction of Cu(ClO₄)₂·6H₂O with 2-pyridylpyrazole (2-PypzH) and *t*-butylphosphonic acid in a 2:1:1 stoichiometry in the presence of triethylamine afforded a blue solid

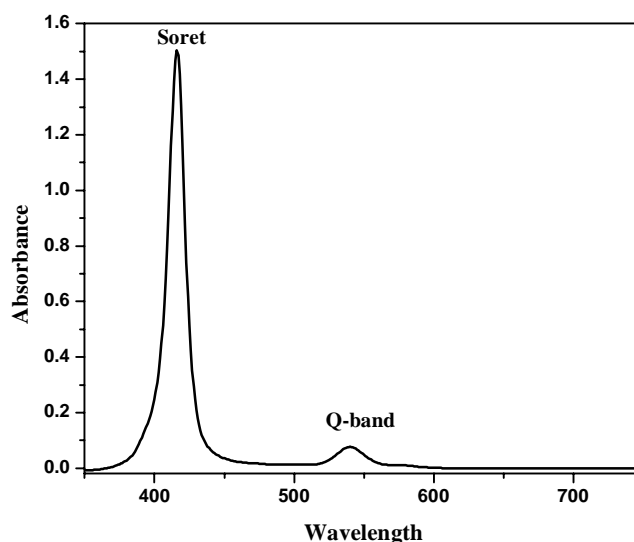


Figure 2. UV-Vis spectrum for **7**.

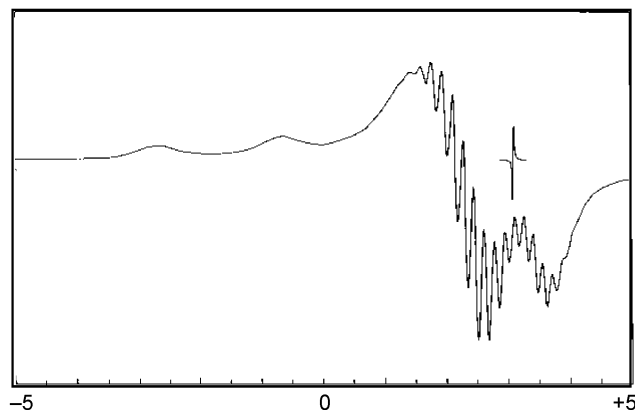
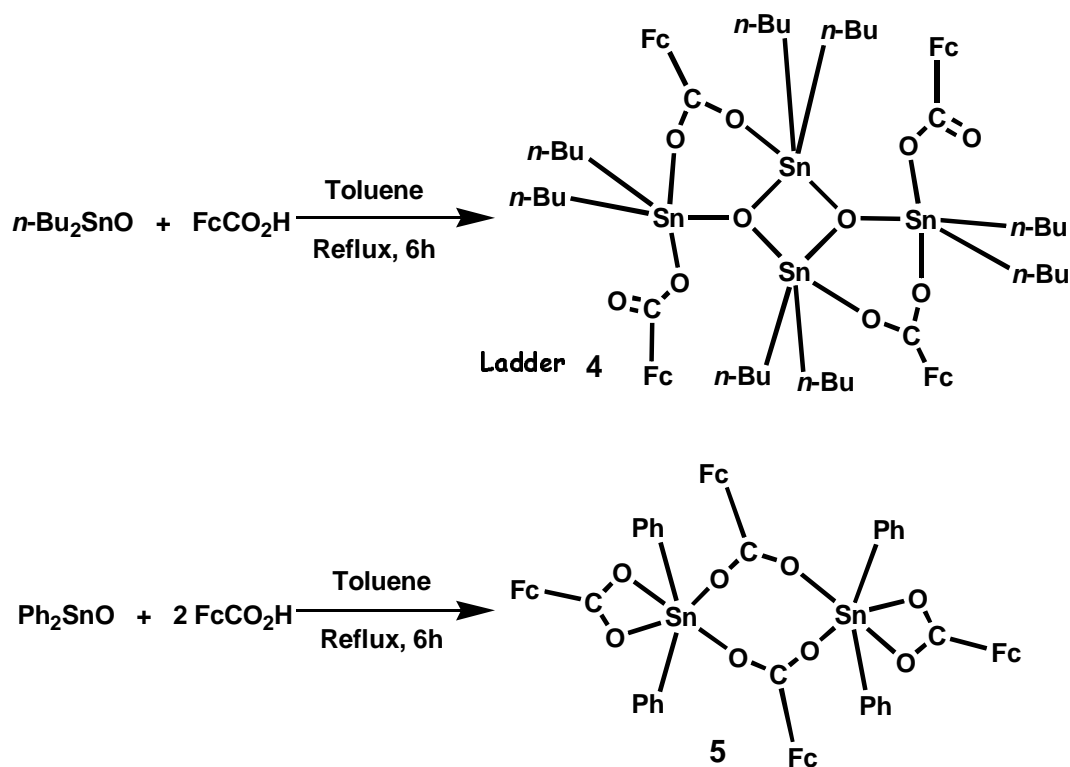
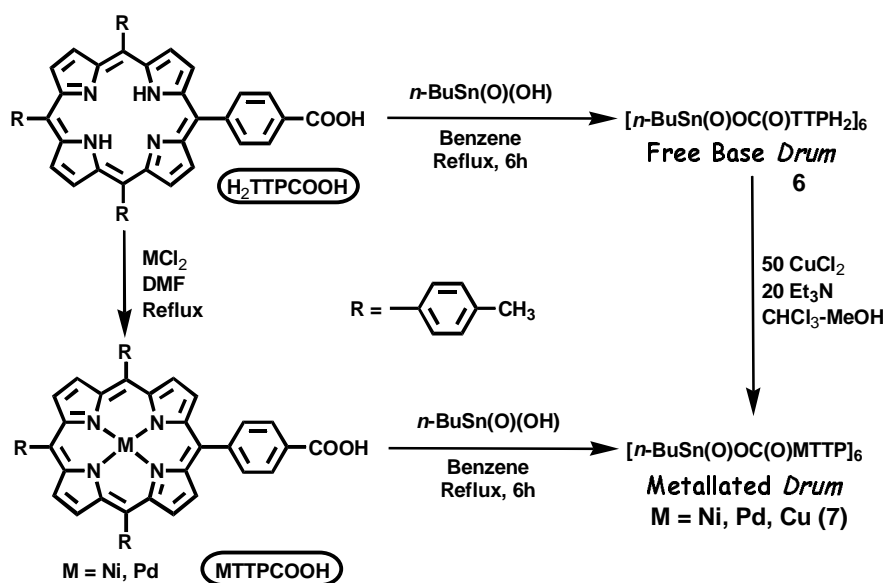


Figure 3. EPR spectrum of **7**.



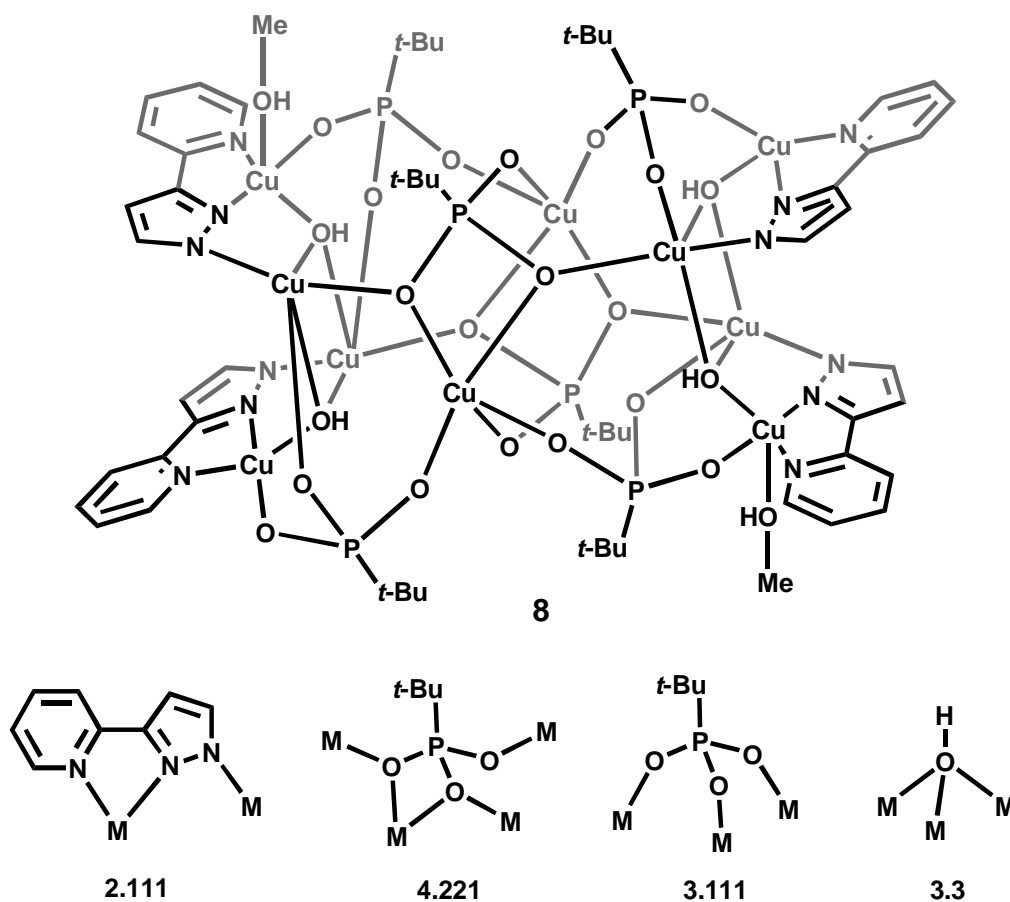
Scheme 7. Synthesis of tetra-ferrocene assemblies 4 and 5.



Scheme 8. Synthesis of hexa-porphyrin drums 6 and 7.

whose molecular structure revealed it to be a decanuclear Cu(II) cage, $[\text{Cu}_5(\mu_3\text{-OH})_2(t\text{-BuPO}_3)_3(2\text{-PyPz})_2(\text{MeOH})_2]_2 \cdot 10\text{MeOH} \cdot 2\text{H}_2\text{O}$ (**8**)¹⁷ containing *t*-butylphosphonate ($t\text{-BuPO}_3^{2-}$), 2-pyridylpyrazolate (2-PyPz^-) and hydroxide ligands (HO^-) (scheme 9). The coordination behaviour (Harris No-

tation)¹⁸ of the individual ligands is also shown in scheme 9. Magnetic measurements on this complex reveal a complex magnetic behaviour. However, overall a strong antiferromagnetic exchange interaction appears to dominate this deca-copper assembly.



Scheme 9. Structure of **8** and ligand coordination modes with Harris notation.

5. Conclusion

We have shown the versatility of the phosphonate ligands for the synthesis of multi-tin and multi-copper assemblies. While the former requires phenolates as the co-ligand, the latter requires nitrogenous ligands such as pyrazoles. The predictable formation of a given type of stannoxane cluster has been conveniently utilized for the synthesis of hexa-ferrocene and hexa-porphyrin architectures. In these assemblies a central Sn_6O_6 core serves to support the functional periphery.

Acknowledgements

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18. Harris notation describes the binding mode as $[X.Y_1Y_2Y_3 \dots Y_n]$, where X is the overall number of metals bound by the whole ligand and each value of Y refers to the number of metal atoms attached to the different donor atoms. See: Coxall R A, Harris S G, Henderson D K, Parsons S, Tasker P A and Winpenny R E P 2000 *J. Chem. Soc., Dalton Trans.* 2349