

Cyclocarbophosphazene-Containing Tetrameric Assemblies Formed by the Mediation of P–O–P and P–O–Cu Linkages

Vadapalli Chandrasekhar,* Ramachandran Azhakar, Venkatasubbaiah Krishnan, Arunachalampillai Athimoolam, and Balasubramanian Murugesu Pandian

Department of Chemistry, Indian Institute of Technology—Kanpur, Kanpur-208 016, India

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Cyclophosphazenes are among the most well studied and well understood inorganic ring systems.¹ In contrast, heterocyclophosphazenes, where one or more phosphorus atoms of the cyclophosphazene ring are replaced by carbon,² sulfur,³ metal,⁴ or a metalloid,⁴ have received much less attention. However, the available studies already indicate a crucial and influential role of the heteroatom on the properties of the inorganic ring. For example, while the ring opening polymerization (ROP) of $N_3P_3Cl_6$ occurs at 250 °C, the ROP of the cyclocarbophosphazene, $N_3P_2CCl_5$, occurs at 120 °C.⁵ Similarly, substantial reactivity differences between cyclophosphazenes and cyclocarbophosphazenes have been noted.^{2c}

We and others have been interested for some time in the use of cyclophosphazene rings as ligands toward transition and main group metals.⁶ In particular, we have shown the versatile nature of the cyclophosphazene ring to act as a support for the assembly of multi-site coordination ligands.^{6a} In view of this interest, we looked at carbophosphazenes as possible scaffolds for the construction of versatile multi-dentate ligands. In anticipation of varying reactivity at the phosphorus and carbon centers, we have prepared the multi-site coordination ligand, $[\{NP(3,5\text{-Me}_2\text{Pz})_2\}\{NC(3,5\text{-Me}_2\text{Pz})\}_2]$ (**2**) from $[\{NPCl_2\}\{NCCl_2\}]$ (**1**) (see Supporting Information) and studied its interaction with $Cu(II)X_2$ ($X = Cl, Br$). We report, herein, the isolation of unprecedented examples of cyclocarbophosphazene-containing tetramers $[\{N_3C_2(3,5\text{-Me}_2\text{Pz})_2P(O)\cdot CuCl\}_2O]_2$ (**3**) and $[\{N_3C_2(3,5\text{-Me}_2\text{Pz})_2P(O)\cdot CuBr_2\}_2\{N_3C_2(3,5\text{-Me}_2\text{Pz})_2P(O)\cdot Cu(3,5\text{-Me}_2\text{PzH})\}_2O]_2$ (**4**). The cyclocarbophosphazene units in these tetramers are held together by P–O–P and P–O–Cu linkages. Such structural entities are unprecedented, to the best of our knowledge, among heterocyclophosphazenes.

The reaction of **2** with $CuCl_2$ or $CuBr_2$ afforded the tetranuclear copper(II) complexes **3** and **4** (Figures 1 and 2). The formation of **3** and **4** is totally reproducible and involves a regioselective hydrolytic P–N bond cleavage reaction involving the phosphorus–pyrazole unit. Even adventitious amount of moisture is sufficient for this reaction. Interestingly, **2** itself is not hydrolytically sensitive as confirmed by ^{31}P NMR experiments (see Supporting Information). Recent literature precedents point to metal-assisted P–N^{6j,7} (and in one instance C–N bond hydrolysis)^{7c} bond cleavage processes. Very recently, Cavell and co-workers have reported a water-induced rearrangement of a platinocyclic carbene to a platinocyclic carbophosphazene.⁸

The molecular structures of **3** and **4** have many common features. Because of this, only the molecular structure of **3** is described in detail. The molecular structure of **3** is shown in Figure 1.

Compound **3** contains four metalated carbophosphazene units that are linked to each other by P–O–P and P–O–Cu bonds. Each of the four carbophosphazenes present in **3** is monoanionic and binds to one copper atom. However, there are two types of copper centers in the molecule. While the terminal copper atoms (Cu1 and Cu1*) are four-coordinate (3N,1Cl), the central copper atoms (Cu2

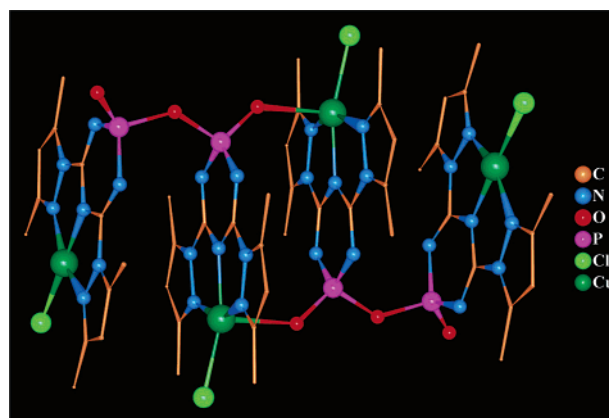


Figure 1. DIAMOND view of **3**; hydrogen atoms have been removed for clarity.

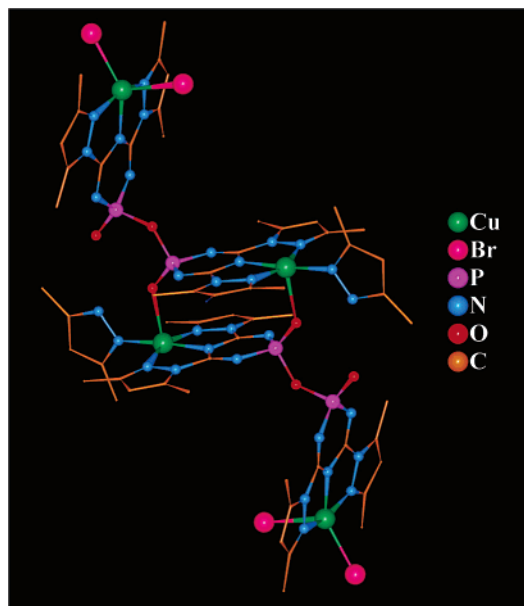


Figure 2. Diamond view of **4**; hydrogen atoms have been removed for clarity.

and Cu2*) are five-coordinate (3N,1O,1Cl). The carbophosphazene ring binds to all the copper atoms in a *nongeminal* N_3 mode. This is accomplished by the involvement of the two pyrazole nitrogens substituted on carbon and the ring nitrogen atom present between the carbon centers (Figure 1). The geometry around these copper atoms is approximately planar. While the coordination around Cu2 and Cu2* is similar to that of the terminal copper atoms (Cu1 and Cu1*), these central copper atoms contain an additional coordination through the phosphoryl, P=O, unit. The coordination geometry around Cu2 and Cu2* is approximately square pyramidal with the

oxygen atom of the phosphoryl group occupying the apical position. In **3**, the average P–N distance is 1.645(5) Å, which is longer than those reported for other substituted cyclocarbophosphazenes.⁹ Two types of C–N bond distances are found in **3** [av. 1.287(7) and 1.354(7) Å], indicating that the anionic charge is not equally delocalized over the entire N–C–N–C–N segment. The longer C–N bonds are associated with the ring nitrogen atom involved in coordination to the metal. The overall molecular structure of **3** comprises four planar carbophosphazene skeletons arranged one over the other (with an alternate translational displacement) in a “rack”-like arrangement (Figure 1). Two types of linkages assist the assembly of **3**. The first linkage is in the form of a P–O–P covalent bond, which binds two carbophosphazenes. It is reasonable to presume that the P–O–P linkage is formed by a condensation of two hydrolyzed carbophosphazene units. Accordingly, two types of P–O bond distances [av. 1.467(4) and 1.602(4) Å] are observed for the terminal carbophosphazene rings in **3**. One of the P=O groups of each such dimeric unit, containing the P–O–P bond, is involved in coordination to one copper atom each (P–O–Cu) to generate the tetrameric assembly of **3**. The P–O–Cu linkage also leads to the formation of a central macrocycle comprised of two cyclocarbophosphazenes that are bound *end-to-end*. The supramolecular architecture of **3** is interesting. The pyrazolyl units of **3** are involved in intermolecular C–H⋯O interactions with P=O moieties.^{10a} Further, intermolecular π – π stacking of the pyrazolyl groups also is prominent.^{10b} The cumulative effect of these interactions is the formation of a two-dimensional network (see Supporting Information).

The molecular structure of **4** is shown in Figure 2. Although the gross structural features of compound **4** are similar to that of **3**, there are subtle variations. First, the molecular structure contains a central macrocycle assembled from P–O–Cu-linked end-to-end bound carbophosphazenes. The other two carbophosphazenes in **4** are arranged in a *trans* manner with respect to the central macrocycle (Figure 2). Because of this, the separation between the two terminal copper atoms (Cu1–Cu1*) is ~17.9 Å (cf., in **3**, this separation is ~12.5 Å). Other differences in the structure of **4**, *vis-à-vis* **3**, relate to the coordination environment around copper atoms. While each carbophosphazene persists with the *nongeminal* N₃ coordination mode to each copper, the terminal copper atoms Cu1 and Cu1* have two other bromide ligands leading to five coordination (3N,2Br), where each copper atom is in a distorted square pyramidal geometry. The central copper atoms Cu2 and Cu2* in **4** are also five-coordinate (4N,1O). One free pyrazole ligand, generated in situ, during the metalation of **2**, takes the fifth coordination site. The coordination geometry around Cu2 and Cu2* is also distorted square pyramidal with the phosphoryl oxygen taking the apical coordination site.

The crystal packing of **4** shows channel-like voids when viewed along the crystallographic *z*-axis (see Supporting Information). These channels are occupied by disordered solvent dichloromethane molecules. The supramolecular interactions are mediated through C–H⋯O interactions.^{10a}

In conclusion, we report the synthesis and structures of unprecedented cyclocarbophosphazene-containing tetramers, where the individual six-membered carbophosphazene inorganic rings are tethered together by P–O–P and P–O–Cu bonds.

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Supporting Information Available: CIF files for **3** and **4**. Synthesis, spectral, and analytical data for **2–4**. Schemes S1–S3 and Figures S1–S9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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