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# Cyclophosphazene-Supported Tetranuclear Copper Assembly Containing 15 Contiguous Inorganic Rings

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The cyclophosphazene hydrazide *gem*-$N_3P_3Ph_2[N(Me)NH_2]_4$ was reacted with *o*-hydroxybenzaldehyde to afford the multisite coordination ligand *gem*-$N_3P_3Ph_2[N(Me)N{=}CHC_6H_4\text{-}2\text{-}OH]_4$ ($LH_4$). The latter reacted with copper(II) salts to afford a novel tetranuclear copper assembly $\{N_3P_3Ph_2[N(Me)N{=}CHC_6H_4\text{-}2\text{-}O]_4Cu_2\}_2$, which contains, remarkably, 15 contiguous inorganic rings.

The utility of cyclophosphazenes as robust platforms for the construction of multisite coordination ligands has been recognized, and this area has been receiving attention in recent years.[1] This application stems from the rich nucleophilic substitution chemistry of chlorocyclophosphazenes.[2,3] Accordingly, a large variety of ligands have been built by appropriate substitution at the phosphorus centers of the cyclophosphazene ring.[4–11] The versatility of the cyclophosphazene-based ligands would be considerably enhanced if an existing ligand can be further elaborated into a new system. Our recent experience of acyclic phosphorus hydrazones[12] has encouraged us to apply such a methodology to the cyclophosphazene ring systems. We had chosen cyclophosphazene hydrazides for this purpose, and previously we have reported the metalation of *spiro*-$N_3P_3[O_2C_{12}H_8][N(Me)NH_2]_4$.[13] In all of the cases that we examined, we were able to obtain only 2:1 (L:M) mononuclear complexes where the central metal ion $Co^{III}$, $Ni^{II}$, $Zn^{II}$, or $Cd^{II}$ was bound by two cyclophosphazene ligands, each as a non-*gem*-$N_3$ donor.[13] Anticipating a change in the coordination response upon elaborating the tetrahydrazide, we prepared *gem*-$N_3P_3Ph_2[N(Me)N{=}CHC_6H_4\text{-}2\text{-}OH]_4$ ($LH_4$, **3**) and examined its metalation with copper(II) salts. In contrast to the mononuclear complexes obtained in the reactions of the parent hydrazide, metalation of $LH_4$ with copper(II) salts affords a novel tetranuclear copper(II) assembly, $\{N_3P_3Ph_2[N(Me)N{=}CHC_6H_4\text{-}2\text{-}O]_4Cu_2\}_2$ (**4**). Additionally, **4** also is structurally quite interesting because it represents a one-pot synthesis of a polycyclic system where 15 contiguous inorganic rings are attached to each other.

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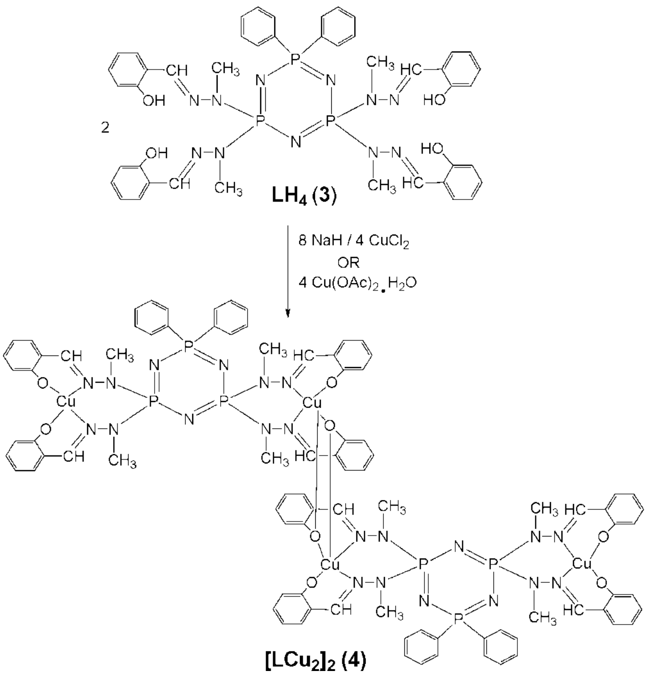
**Scheme 1**



The reaction of *gem*-$N_3P_3Ph_2Cl_4$ (**1**) with *N*-methylhydrazine afforded *gem*-$N_3P_3Ph_2[N(Me)NH_2]_4$ (**2**). The tetrahydrazide (**2**) is formed by a regiospecific reaction and contains four reactive –$NH_2$ groups.[14] Condensation of **2** with *o*-hydroxybenzaldehyde affords the tetrahydrazone **3** (see Scheme S1 in the Supporting Information). Compounds **1**–**3** are characterized by an $AX_2$ type of $^{31}P\{^1H\}$ NMR spectrum. The $^{31}P$ NMR chemical shift involving the reactive phosphorus center moves downfield and then again upfield upon conversion of **1** into **2** and then into **3** [$\delta$ $PCl_2$ (**1**) 18.3 ppm; $\delta$ $P[N(Me)NH_2]_2$ (**2**) 28.1 ppm; $\delta$ $P[N(Me)N{=}CHC_6H_4\text{-}2\text{-}OH]_2$ (**3**) 13.1 ppm]. Both **2** and **3** show parent ion peaks in their fast atom bombardment (FAB) mass spectra (see the Supporting Information).

The reaction of **3** with sodium hydride followed by anhydrous $CuCl_2$ afforded **4** in about 70% yield (Scheme 1). **4** is also formed in a *direct* reaction involving $LH_4$ and $Cu(OAc)_2 \cdot H_2O$ (see the Supporting Information). The formation of **4** can be understood readily. The two hydrazone arms present on either side of the cyclophosphazene ring are deprotonated, and the resulting tetraanionic ligand $[L]^{4-}$ encapsulates two $Cu^{II}$ ions in a concerted coordination action to afford $LCu_2$, which is present in the solid state as a centrosymmetric dimer, $[LCu_2]_2$ (Figure 1). The FAB mass spectrum of **4** shows a peak at *m/z* 1009 corresponding to $[LCu_2]^+$. The optical spectrum of **4** is characterized by the presence of ligand absorption (230 and 266 nm), ligand (phenolate oxygen)–metal charge transfer (383 nm), and d–d absorption (610 nm).[17a] The two distinct copper sites present in **4** are not resolved in the electron paramagnetic resonance spectrum of **4** (recorded as $CH_2Cl_2$/toluene glass at liquid-nitrogen temperature). An axial pattern is observed with $g_\parallel > g_\perp$ ($g_\parallel = 2.216$, $g_\perp = 2.04$, $A_\parallel^{Cu} = 168$ G, $A_\perp^{N} = 14.65$ G, and $A_\perp^{Cu} = 29.3$ G). The observed *g* values are consistent with a $d_{x^2-y^2}$ ground state for the $Cu^{II}$ ion.[15] The coordination environment around the two terminal Cu atoms is comprised of two phenolate O atoms and two imino N atoms (Figure 2a). The coordination geometry may be described as distorted square planar, where the ligands are arranged in a cis orientation (Figure 2). The average Cu–N distance is 1.972(5) Å and is slightly longer than the average Cu–O distance, 1.905(5) Å. Each of terminal Cu atoms is part of three interconnected six-membered rings (Figure 1). The central Cu atoms (Cu2 and Cu2*) are connected to each other by the $\mu_2$-bridging phenolate atoms O3 and O3* (Figure 2b). The resulting $Cu_2O_2$ four-membered ring is nearly planar.

The Cu2–O3* distance is 2.557(2) Å, and although it is longer than a normal Cu–O distance, it is much shorter than the sum of the van der Waals radii of Cu and O (~2.90 Å).[16] The formation of such $M_2O_2$ dimers, although not documented in cyclophosphazene–metal complexes, is quite well-known.[17] The coordination environment around the central Cu atoms is square-pyramidal, with the bridging O atoms occupying the apical position.

Complexation with Cu causes the cyclophosphazene ring to be puckered. The atoms P2 and N3 move out of the mean plane of the $N_3P_3$ ring by 0.18 Å, while P3 and N1 are similarly displaced in the opposite direction.

A remarkable feature of the tetranuclear assembly **4** is the presence of 15 interconnected inorganic rings (all of the rings are labeled in Figure 1). Of these, only two (the cyclophosphazene rings) are originally present and the rest are simultaneously generated coincident with the assembly of **4**. Of the 15 rings, one is four-membered ($Cu_2O_2$), which has on either side of it seven six-membered rings (Figure 1). Except for the central four-membered ring, the rest are nonplanar (see the Supporting Information). The overall architecture of the polycyclic assembly is Z-shaped (Figure 1), with the end-to-end copper distance Cu1–Cu1* being 18.2 Å.

Variable-temperature magnetic measurements on **4** reveal an antiferromagnetic behavior. At room temperature, the observed $\mu_B$ (per Cu) is 1.92 $\mu_B$. As the temperature is lowered, a gradual decrease in $\chi_M T$ is noticed, consistent with antiferromagnetic behavior.

In conclusion, we have shown that modification of cyclophosphazene ligands into more elaborate and complex coordinating systems is feasible by an appropriate design. In the current example, elaboration of a cyclophosphazene tetrahydrazide affords a novel multisite coordinating ligand, $LH_4$, which readily generates a polycyclic tetranuclear copper(II) assembly. The versatility and diversity of cyclophosphazene-based ligands can be considerably enhanced by

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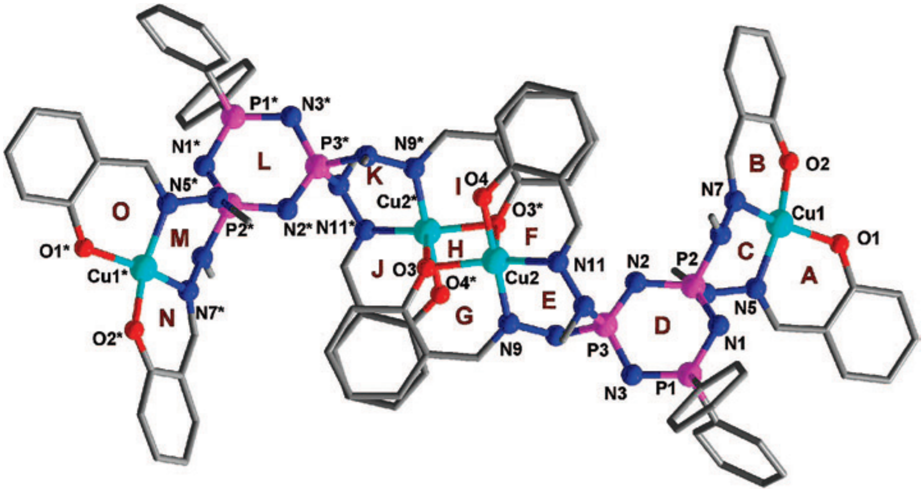

**Figure 1.** Diamond picture of compound **4**. H atoms are omitted for clarity.

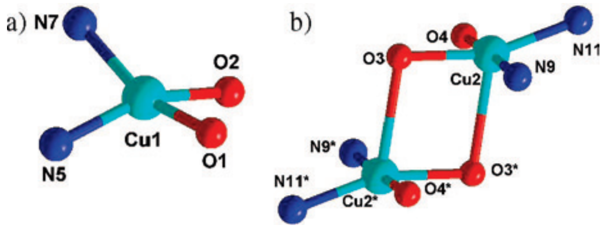

**Figure 2.** (a) Coordination environment around the terminal atom Cu1. (b) Coordination environment around the central atoms Cu2 and Cu2*. Selected bond distances (Å) around Cu1 and Cu2: Cu1−O2 1.882(5); Cu1−N5 1.927(5); Cu1−O1 1.928(4); Cu1−N7 2.016(5); Cu2−O4 1.915(4); Cu2−N9 1.958(5); Cu2−O3 1.974(4); Cu2−N11 1.985(5); Cu2−O3* 2.553(5). Important bond angles (deg) around Cu1 and Cu2: O2−Cu1−N5 156.3(2); O2−Cu1−O1 89.6(2); N5−Cu1−O1 92.2(2); O2−Cu1−N7 94.2(2); N5−Cu1−N7 93.0(2); O1−Cu1−N7 157.79(19); O4−Cu2−N9 177.18(18); O4−Cu2−O3 88.69(19); N9−Cu2−O3 90.9(2); O4−Cu2−N11 90.8(2); N9−Cu2−N11 90.5(2); O3−Cu2−N11 160.65(18); N9−Cu2−O3* 89.01(2); N11−Cu2−O3* 116.37(2); O4−Cu2−O3* 88.17(2); O3−Cu2−O3* 82.94(2).

appropriate elaboration strategies provided that they are not detrimental to the stability of the inorganic ring. We are exploring further applications of this paradigm.

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**Supporting Information Available:** Experimental section, crystal data, magnetic measurement data, and mean-plane information. This material is available free of charge via the Internet at http://pubs.acs.org.

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