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Diamondoid-Type Copper Coordination Polymers Containing Soft Cyclodiphosphazane Ligands

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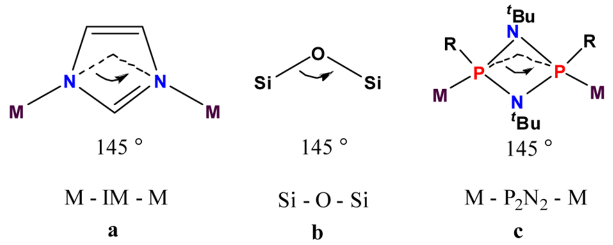
Supporting Information

ABSTRACT: Three novel coordination polymers have been synthesized by reacting *cis*- and *trans*-alkyne-appended cyclodiphosphazanes with CuX (X = Br, I) salts. The reaction of *cis*-$[(\mathrm{PhC{\equiv}CP})_2(\mu\text{-N}^t\mathrm{Bu})_2]$ (**1**) with CuBr in a 1:3 molar ratio gave a 3D coordination polymer, $[\{\mathrm{Cu}_4(\mu_3\text{-Br})_4\}\{(\textit{cis-}(\mathrm{PhC{\equiv}CP})_2(\mu\text{-N}^t\mathrm{Bu})_2)\text{-}\mathrm{Cu}_4(\mu_2\text{-Br})_4(\textit{cis-}(\mathrm{PhC{\equiv}CP})_2(\mu\text{-N}^t\mathrm{Bu})_2)\}_4]_n$ (**3**), having diamondoid topology with an unprecedented copper alkyne coordination, whereas the reaction of **1** with CuI in a 1:4 molar ratio afforded a 1D polymeric complex, $[\{\mathrm{Cu}_4(\mu_3\text{-I})_4\}(\mathrm{NCCH}_3)_2\{\textit{cis-}(\mathrm{PhC{\equiv}CP})_2(\mu\text{-N}^t\mathrm{Bu})_2\}_2]_n$ (**4**). In contrast, the reaction of *trans*-$[(\mathrm{PhC{\equiv}CP})_2(\mu\text{-N}^t\mathrm{Bu})_2]$ (**2**) with CuI was found to be independent of stoichiometry and afforded a 3D coordination polymer, $[\{\mathrm{Cu}_4(\mu_3\text{-I})_4\}\{\textit{trans-}(\mathrm{PhC{\equiv}CP})_2(\mu\text{-N}^t\mathrm{Bu})_2\}_2]_n$ (**5**), exclusively.

Porous coordination polymers (PCPs) or metal−organic frameworks (MOFs) are attracting increasing attention because of their structural diversities and novel framework topologies.[1] In comparison with metal carboxylate and bipyridine-based coordination polymers, phosphine-based PCPs are less studied, and only a handful of 2D and 3D frameworks have been reported so far.[2] The use of soft Lewis base linkers derived from phosphine ligands is scarce mainly for two reasons: (i) the lack of phosphine linkers with a rigid framework as the pyramidal geometry at the P atom and free rotation about the P−C bonds, allowing a range of accessible orientations of lone pairs and bringing ambiguity to the coordination behavior[3] and (ii) the dearth of soft Lewis acidic tetrahedral metal ions/clusters that can act as connecting nodes in the formation of 3D coordination polymers.

One of the most successful methods employed in the synthesis of PCPs is the 4 + 2 strategy involving tetrahedral nodes and ditopic linkers. Cyclodiphosphazanes of the type $[\mathrm{XP}(\mu\text{-NR})]_2$ (X = Cl, Br; R = Ph, ^{t}Bu) are saturated four-membered ring systems with alternating P and N atoms in the cyclic skeleton.[4] The cis orientation of the phosphorus lone pairs makes them important ditopic linkers in the synthesis of metallomacrocycles and coordination polymers.[5] In addition to the rigidity imparted by the cyclic $\mathrm{P}_2\mathrm{N}_2$ ring, a certain degree of flexibility can be introduced in these linkers by changing the steric nature of the phosphorus substituents. In the naturally occurring aluminosilicates, the ditopic linker (O^{2-}) makes an angle of 145° in Si−O−Si(Al) linkages, and the same is the case with zeolitic imidazolate frameworks (ZIFs; M−IM−M = 145°).[6] Recently, we have reported the synthesis of the first phosphine-based zeotype frameworks, where the cyclodiphosphazane ligand acts as a ditopic linker exhibiting an angle of 145° (Chart 1).[7] This demonstrates the potential of cyclodiphosphazanes as soft ditopic linkers in the construction of MOFs.

Chart 1. Bridging Angles in ZIFs (a), Zeolites (b), and Cyclodiphosphazanes (c)



Of the monovalent soft Lewis acidic group 11 metals, the copper(I) salts have attracted much interest because of their novel topological behavior and rich photophysical properties.[8] The tetrameric closed cubane complexes of the type $[\mathrm{Cu}_4(\mu_3\text{-I})_4\mathrm{L}_4]$ (L = monodentate ligand or L4 = two bidentate ligands) have received special attention because of their ability to act as tetrahedral nodes often showing interesting luminescence and thermochromic properties.[9]

After the coordination chemistry of various cyclodiphosphazane systems was studied,[7,10] it was observed that the less bulky substituents on phosphorus increase the $\mathrm{M{-}P_2N_2{-}M}$ (M = metal center) angle, making it ideally suited for the synthesis of large macrocycles and coordination polymers. Thus, less sterically demanding alkynyl-appended cyclodiphosphazanes, *cis*-$[(\mathrm{PhC{\equiv}CP})_2(\mu\text{-N}^t\mathrm{Bu})_2]$ (**1**) and *trans*-$[(\mathrm{PhC{\equiv}CP})_2(\mu\text{-N}^t\mathrm{Bu})_2]$ (**2**), were chosen for examination of their ligating properties with cuprous halides (Chart 2). The inclusion of alkynyl moieties in the ligands was to provide additional donor sites because such groups have led to intriguing structures by coordination to the metal centers.[11] Herein, we report the synthesis of three different copper(I) coordination polymers of alkyne-appended cyclodiphosphazanes involving $[\mathrm{Cu}_4(\mu_3\text{-I})_4]$ clusters as tetrahedral nodes.

Slow diffusion of an acetonitrile solution of CuBr into a solution of **1** in dichloromethane in a 1:3 molar ratio, at room

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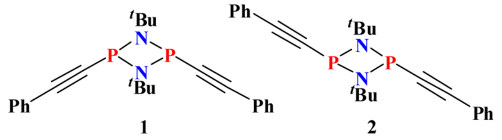
Chart 2. *cis*- and *trans*-Alkynylcyclodiphosphazanes (1 and 2, Respectively)



temperature, afforded yellow crystals of $[\{Cu_4(\mu_3\text{-}Br)_4\}\{(cis\text{-}(PhC{\equiv}CP)_2(\mu\text{-}N^tBu)_2)Cu_4(\mu_2\text{-}Br)_4(cis\text{-}(PhC{\equiv}CP)_2(\mu\text{-}N^tBu)_2)\}_4]_n$ (3). The $^{31}P\{^1H\}$ NMR spectrum of 3 in dimethyl sulfoxide DMSO-d_6 displayed a broad single resonance at 98.9 ppm with an upfield coordination shift of 65.1 ppm (for **1**, δ_P = 164 ppm). The fundamental building unit comprises of one ligand **1**, three Cu atoms, three Br atoms, and one acetonitrile molecule. The framework is made up of two different types of Cu_4Br_4 moieties: one is a $[Cu_4(\mu_3\text{-}Br)_4]$ cubane cluster, whereas the other is an eight-membered stairstep $[Cu_4(\mu_2\text{-}Br)_4]$ unit. The overall molecular framework is made up of $[Cu_4(\mu_3\text{-}Br)_4]$ clusters acting as tetrahedral building blocks and stairstep $[Cu_4(\mu_2\text{-}Br)_4]$ units flanked between two η^1-coordinated P_2N_2 rings (having dangling uncoordinated P atoms on both ends) as ditopic linkers (Figure 1a). One of the prominent features of this framework is the unprecedented coordination of two diagonally disposed Cu^I ions of the stairstep $[Cu_4(\mu_2\text{-}Br)_4]$ units to the alkynyl groups on the P_2N_2 rings. The stairstep $[Cu_4(\mu_2\text{-}Br)_4]$ unit consists of two different sets of Cu^I ions: one set of tetrahedral Cu^I ions is coordinated by two Br^- ions, one P from the P_2N_2 ring and an acetonitrile molecule (Figure 1b). The other set of Cu^I ions is bonded to the alkyne bond of the phenyl acetylene group and two Br^- ions, thereby displaying distorted tetrahedral geometry. The Cu1−Br1 and Cu1−Br2′ and the Cu2−Br1 and Cu2−Br2 distances are 2.6038(3) and 2.4917(2) Å and 2.4068(2) and 2.3641(2) Å, respectively. The Cu⋯Cu distances in the $[Cu_4(\mu_3\text{-}Br)_4]$ cluster are in the range 3.05−3.09 Å, whereas the Cu−P bond distance is 2.1823(3) Å. The copper−alkyne interaction is weak, as revealed by the short C−C bond distance of 1.22(9) Å, but strong enough to distort the phenyl acetylene skeleton from linearity by 13.5°.[11c] The size of the adamantanoid cages in **3** is 29.8 × 35.1 × 42.3 $Å^3$ with an edge length of 18.31 Å (Figure 1c). A 3-fold interpretation is observed in the framework **3** (Figure S7 in the Supporting Information, SI).

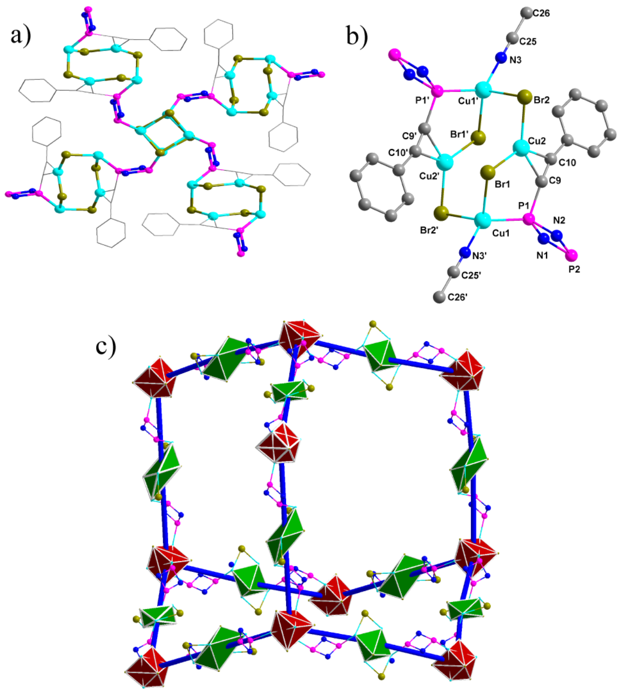


Figure 1. (a) Tetrahedral building blocks in **3**. (b) Eight-membered stairstep $[Cu_4(\mu_2\text{-}Br)_4]$ units. (c) Adamantanoid cages in **3** with dimensions of 29.8 × 35.1 × 42.3 $Å^3$. Red polyhedra represent $[Cu_4(\mu_3\text{-}Br)_4]$ cubane clusters and green polyhedra stairstep $[Cu_4(\mu_2\text{-}Br)_4]$ units. The *tert*-butyl and alkynyl groups have been omitted for clarity.

The reaction of **1** with CuI in a 1:4 molar ratio in a mixture of dichloromethane and acetonitrile yielded a 1D coordination polymer, $[\{Cu_4(\mu_3\text{-}I)_4\}(NCCH_3)_2\{cis\text{-}(PhC{\equiv}CP)_2(\mu\text{-}N^tBu)_2\}_2]_n$ (**4**), as a yellow solid. The $^{31}P\{^1H\}$ NMR spectrum of **4** in DMSO-d_6 showed a broad single resonance at 96.6 ppm. In the ^1H NMR spectrum, the *tert*-butyl groups resonate at 1.49 ppm, whereas the coordinated acetonitrile molecules resonate at 2.06 ppm. In the molecular structure of **4**, the asymmetric unit consists of two crystallographically unique $[Cu_4(\mu_3\text{-}I)_4]$ clusters. In each $[Cu_4(\mu_3\text{-}I)_4]$ cluster, the fourth coordination site on diagonally disposed Cu^I ions is bonded to acetonitrile molecules, whereas the other two Cu^I ions are bonded to the bridging P_2N_2 ring, as shown in Figure 2a, thus forming a 1D polymeric strand. All four Cu^I centers adopt distorted tetrahedral geometries, with the average Cu−I bond distances in the range 2.680−2.711 Å. The Cu⋯Cu distances are in the range 2.754(4)−3.251(9) Å.

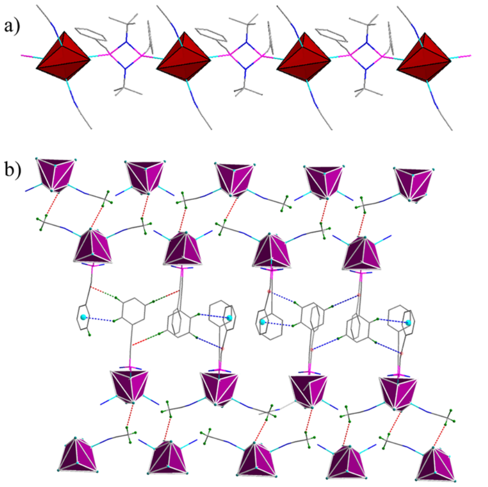


Figure 2. (a) 1D polymeric chain in **4**. (b) 3D framework of **4** arising because of secondary interactions.

The two crystallographically independent $[Cu_4(\mu_3\text{-}I)_4]$ clusters in the asymmetric unit correspond to two different 1D polymeric strands. These two strands are interweaved with two similar strands from the upper layer in a head-to-tail manner with C−H⋯π as well as nonbonding aromatic interactions, as depicted in Figure 2b. Two phenyl H atoms from each layer show CH⋯π (alkyne) interactions with the alkynyl moiety from the other layer in a head-to-tail fashion (C−H⋯π = 3.04−3.05 Å; C−H⋯π = 157.4−163.8°). The distance of the CH⋯π T-shape stacking interaction is 3.23 Å. Furthermore, in the crystal lattice of **4**, weak hydrogen bonding is observed between the acetonitrile molecules from one layer with iodide ions from the adjacent layer (H⋯I = 3.157−3.178 Å; C−H⋯I = 158.4−167.36°).

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The reaction of **2** with CuI in a 1:2 molar ratio afforded the 3D coordination polymer $[\{Cu_4(\mu_3\text{-}I)_4\}\{trans\text{-}(PhC{\equiv}CP)_2(\mu\text{-}N^tBu)_2\}_2]_n$ (**5**). Single crystals of **5** were obtained by slow diffusion of a acetonitrile solution of CuI into a solution of **2** in dichloromethane in a 1:2 molar ratio at room temperature. The product formation was found to be independent of the stoichiometry of the reactants because 1:3 and 1:4 reactions also yielded the same product. The solid-state ^{31}P CP-MAS NMR spectrum of **5** showed a 1:1:1:1 quartet at 95 ppm originating from the $^{63,65}Cu-^{31}P$ coupling. The spectral features are in agreement with similar $[Cu_4(\mu\text{-}I)_4]$-bound complexes $[Cu_4I_4(Ph_2PCH_2CH{=}CH_2)_4]$ and $[Cu_4I_4(Ph_2P(CH_2)_2Si(OH)_2OSi(OH)_2(CH_2)_2PPh_2)_2]$.[9a,b] The asymmetric unit in compound **5** consists of one crystallographically unique Cu^I ion, one iodide ion, and half of the P_2N_2 ring. The overall 3D framework consists of $[Cu_4(\mu\text{-}I)_4]$ tetrahedral building blocks linked in all four directions by ditopic P_2N_2 rings (**2**) to form a 3D diamondoid-type network. In the tetrahedral $[Cu_4(\mu_3\text{-}I)_4]$ clusters, each Cu^I ion is coordinated to three μ_3-I ions and one P atom from the ditopic ligand (**2**) with Cu−I and Cu−P distances of 2.6579(1)−2.6939(1) and 2.2311(7) Å, respectively (Figure 3a). The size of the adamantanoid cage is 17 × 22 × 26 $Å^3$ with an edge length of 10.1 Å, which is smaller in comparison to that of framework **3** (Figure 3b). The Cu···Cu distances are in the range 3.0412(3)−3.0542(1) Å.

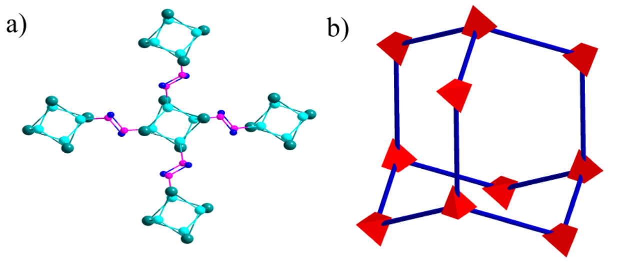

Figure 3. (a) Tetrahedral building blocks in **5** and (b) adamantanoid cage in **5** with dimensions 17 × 22 × 26 $Å^3$. Red polyhedra represent $[Cu_4(\mu_3\text{-}I)_4]$ cubane clusters. All of the *tert*-butyl and alkynyl groups have been omitted for clarity.

In summary, less sterically bulky alkyne-appended cyclodiphosphazane ligands upon treatment with CuX salts afforded different coordination polymers. The reaction between **1** and CuBr in 1:3 molar ratios afforded a 3D framework (**3**) having alternating tetrahedral $[Cu_4(\mu_3\text{-}Br)_4]$ clusters and stairstep $[Cu_4(\mu_2\text{-}Br)_4]$ units with diamondoid topology. Additionally, the alkyne groups in the P_2N_2 ring showed unprecedented copper(I) alkyne coordination. The reaction of **2** with CuI was found to be independent of the stoichiometry of the reactants affording 3D framework **5**, exhibiting diamondoid topology. In all cases, $[Cu_4(\mu_3\text{-}X)_4]$ clusters act as tetrahedral nodes and cyclodiphosphazane ligands act as ditopic linkers. These results further demonstrate the versatile coordinating properties of cyclodiphosphazane derivatives.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray data in CIF format, experimental details, ^{31}P NMR spectra, and additional figures and tables. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00525.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Tranchemontagne, D. J.; Ni, Z.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5136−5147. (b) Kitagawa, S.; Matsuda, R. *Coord. Chem. Rev.* **2007**, *251*, 2490−2509. (c) Stroppa, A.; Jain, P.; Barone, P.; Marsman, M.; Perez-, J. M.; Cheetham, A. K.; Kroto, H. W.; Picozzi, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 5847−5850.

(2) (a) Tan, X.; Li, L.; Zhang, J.; Han, X.; Jiang, L.; Li, F.; Su, C.-Y. *Chem. Mater.* **2012**, *24*, 480−485. (b) Xu, X.; Nieuwenhuyzen, M.; James, S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 764−767. (c) Bohnsack, A. M.; Ibarra, I. A.; Bakhmutov, V. I.; Lynch, V. M.; Humphrey, S. M. *J. Am. Chem. Soc.* **2013**, 2, 16−19. (d) Zhang, J.; Miller, P. W.; Nieuwenhuyzen, M.; James, S. L. *Chem.—Eur. J.* **2006**, *12*, 2448−2453. (e) Miller, P.; Nieuwenhuyzen, M.; Charmant, J. P. H.; James, S. L. *CrystEngComm* **2004**, *6*, 408. (f) Zhang, J.; Nieuwenhuyzen, M.; Charmant, J. P. H.; James, S. L. *Chem. Commun.* **2004**, 2808−2809.

(3) James, S. L. *Chem. Soc. Rev.* **2009**, *38*, 1744−1758.

(4) (a) Briand, G. G.; Chivers, T.; Krahn, M. *Coord. Chem. Rev.* **2002**, *234*, 237−254. (b) Balakrishna, M. S.; Eisler, D. J.; Chivers, T. *Chem. Soc. Rev.* **2007**, *36*, 650−664. (c) Calera, S. G.; Wright, D. S. *Dalton Trans.* **2010**, *39*, 5055.

(5) (a) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Dalton Trans.* **2009**, 5478−5486. (b) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2006**, *45*, 6678−6683. (c) Suresh, D.; Balakrishna, M. S.; Mague, J. T. *Dalton Trans.* **2008**, 3272−3274. (d) Ananthnag, G. S.; Kuntavalli, S.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2012**, *51*, 5919−5930. (e) Ganesamoorthy, C.; Balakrishna, M. S.; Mague, J. T. *Inorg. Chem.* **2009**, *48*, 3768−3782.

(6) (a) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 10186−10191. (b) Wang, B.; Côté, A. P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2008**, *453*, 207−211.

(7) Siddiqui, M. M.; Mobin, S. M.; Senkovska, I.; Kaskel, S.; Balakrishna, M. S. *Chem. Commun.* **2014**, *50*, 12273−12276.

(8) (a) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625−3648. (b) Crestani, M. G.; Manbeck, G. F.; Brennessel, W. W.; Mccormick, T. M.; Eisenberg, R. *Inorg. Chem.* **2011**, *50*, 7172−7188. (c) Zhang, Y.; He, X.; Zhang, J.; Feng, P. *Cryst. Growth Des.* **2011**, *11*, 29−32.

(9) (a) Perruchas, S.; Le Goff, X. F.; Maron, S.; Maurin, I.; Guillen, F.; Garcia, A.; Gacoin, T.; Boilot, J.-P. *J. Am. Chem. Soc.* **2010**, *132*, 10967−10969. (b) Perruchas, S.; Tard, C.; Le Goff, X. F.; Fargues, A.; Garcia, A.; Kahlal, S.; Saillard, J.-Y.; Gacoin, T.; Boilot, J.-P. *Inorg. Chem.* **2011**, *50*, 10682−10692.

(10) (a) Balakrishna, M. S. *J. Organomet. Chem.* **2010**, *695*, 925−936. (b) Siddiqui, M. M.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2015**, *54*, 1200−1202.

(11) (a) Rao, S.; Mague, J. T.; Balakrishna, M. S. *Dalton Trans.* **2013**, *42*, 11695−708. (b) Naik, S.; Kumaravel, M.; Mague, J. T.; Balakrishna, M. S. *Dalton Trans.* **2014**, 43, 1082−1095. (c) Lorber, C. Y.; Youinou, M.-T.; Kress, J.; Osborn, J. A. *Polyhedron* **2000**, *19*, 1693−1698.