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# Synthesis and crystal structures of coordination polymers, networks and complexes of an adamantane shaped phosphorus-nitrogen cage ligand and cuprous chloride

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# ABSTRACT

Reactions of cuprous chloride with the phosphorus–nitrogen cage ligand 2,4,6,8,9,10-hexamethyl-2,4,6,8,9,10-hexaaza-1,3,5,7-tetraphosphaadamantane,  $P_4(NCH_3)_{6}$ , in acetonitrile form distinct solids depending on the ligand-to-metal ratio. Three structurally characterized compounds include: a solvated 3-D network of formula  $[P_4(NCH_3)_6]_2(CuCl)_3(CH_3CN)_2$ ; a "ladder-type" polymer { $[\mu_2-P_4(NCH_3)_6]_2(CuCl)_2|_{\infty}$ ; and a monomeric complex  $[P_4(NCH_3)_6]_2CuCl$ . Thermal decomposition of the solvated network results in formation of two more materials  $[P_4(NCH_3)_6]_2(CuCl)_3$ , and  $[P_4(NCH_3)_6](CuCl)_2$  that are not isolated from solution reactions. The variety of products isolated based solely on ligand-to-metal ratio suggest that this system participates in solution equilibria common to many phosphorus(III) ligands and multiple solubility equilibria.

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#### 1. Introduction

Great interest is currently focused on metal-organic frameworks (MOFs) as useful materials for their gas storage, catalytic, and optical properties [1–7]. The vast majority of these frameworks are linked by N or O donor atoms. There are considerably fewer examples of coordination polymers and arrays linked by P-donor ligands [8-32]. This report describes some of the coordination polymers and networks formed by the tetradentate, non-chelating ligand, 2,4,6,8,9,10-hexamethyl-2,4,6,8,9,10-hexaaza-1,3,5,7-tetraphosphaadamantane (P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub> or TPHMI in Scheme 1) and cuprous chloride. This ligand can be viewed as a "soft" analogue to hexamethylenetetramine (HMTA), a common bridging ligand in coordination polymers and networks [33]. Preliminary studies have yielded one structurally characterized coordination polymer of  $P_4(NCH_3)_6$  paired with CuI [34]. Here we build on that result with a study of the cuprous chloride system in an effort to develop some principles for rational design of coordination polymers and frameworks bridged by P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub>.

Tetraphosphorushexamethylimide (TPHMI) and its chalcogen derivatives were originally synthesized by Holmes [35,36] and later studied by Cotton and others looking for insight into the  $d\pi$ -p $\pi$  character in the P–N bond [37]. Several other studies showed that TPHMI was a Lewis base that could bind multiple

metal centers [38–40]. The geometric similarities between TPHMI and HMTA, evidence of its ability to bind multiple Lewis acids, and its relatively easy synthesis make  $P_4(NCH_3)_6$  an excellent candidate as a bridging ligand for use in coordination polymers and networks.

# 2. Experimental

All reagents were purchased from Sigma–Aldrich or Fisher/Acros and used without further purification unless otherwise noted. All solvents were dried, distilled, and stored over molecular sieves in the glovebox. With the exception of ligand preparation, all reactions were carried out inside a glovebox (nitrogen atmosphere) to prevent exposure to oxygen or water vapor. Elemental analysis was performed by Columbia Analytical Services, Tucson, AZ. Thermogravimetric analysis was performed on a TAQ50 or 2050 instrument. Typically, 10–20 mg samples were heated from 30 to 700 °C at a ramp rate of 5 °C/min under a 60 mL/min stream of nitrogen.

# 2.1. Ligand preparation $P_4(NCH_3)_6$

Crude ligand was prepared according to the procedure of Holmes and Forstner [36]. Methylamine for the procedure was distilled from a saturated aqueous solution through a column packed with glass beads [41]. The gas was dried further by passing it through a one foot column of potassium hydroxide pellets. The anhydrous methylamine was then condensed into the reaction





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**Scheme 1.** The tetradentate non-chelating ligand P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub>, TPHMI.

vessel at -78 °C. Phosphorus trichloride was added slowly while stirring the mixture with a mechanical stirrer. After warming over two days, the reaction mixture was extracted with dry hexanes, filtered, and evaporated to yield crude product. Vacuum sublimation at 85–100 °C yields pure ligand: <sup>31</sup>P{<sup>1</sup>H} NMR, singlet,  $\delta$  82.2 ppm.

#### 2.2. Preparation of complexes

#### 2.2.1. Synthesis of **1** [P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub>]<sub>2</sub>(CuCl)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub>

A solution of 0.059 g (0.60 mmol) of cuprous chloride in 6.0 mL of dry acetonitrile was added to 6.0 mL of solution containing 0.177 g (0.594 mmol) of  $[P_4(NCH_3)_6]$ . Dropwise addition produced a transient precipitate that redissolved after a few seconds. Once half of the metal solution was added, the precipitate persisted. Large amounts of flocculent precipitate formed as addition was completed. Over a 90 min period, the precipitate settled and became a free-flowing powder in the bottom of the reaction mixture. Vacuum filtration separated a white solid that was washed with dry acetonitrile. Yield: 0.222 g (76%). Samples of **1** dried at 60 °C under vacuum lost 9% of their mass, consistent with the presence of two acetonitrile molecules in the lattice. Elemental *Anal.* Calc. for: C, 19.70; H, 4.34; N, 20.11; Cu, 19.54. Found: C, 19.01; H, 4.45; N, 19.19; Cu, 19.7%.

#### 2.2.2. Synthesis of **2** { $[\mu_2-P_4(NCH_3)_6]_2(CuCl)_2$ }<sub> $\infty$ </sub>

0.607 g (2.04 mmol) of TPHMI was dissolved in 10 mL of dry acetonitrile. This solution was treated with 3 mL of solution containing 0.050 g (0.51 mmol) of CuCl. An initial precipitate redissolved to give a clear solution. The reaction mixture was allowed to stand for two days. At the end of this time a white solid deposited on the bottom and sides of the vial. The product was filtered from the reaction mixture and washed with ether. Yield: 0.091 g (45%). Elemental *Anal.* Calc. for: C, 18.14; H, 4.57; N, 21.17; Cu, 16.00; P, 31.19. Found: C, 18.13; H, 4.79; N, 20.04; Cu, 13.7; P, 29.9%.

# 2.2.3. Crystal growth of **3** [P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub>]<sub>2</sub>CuCl

Single crystals of **3** grew from long standing reaction mixtures where L:M is in excess of 8:1. However, bulk samples of pure **3** were not obtained from reaction mixtures with stoichiometries up to 10:1. Reactions of excess ligand with CuCl were performed as above for **1** and **2**, but all reactants remain in solution. Removal of solvent under vacuum yields a white solid that is mostly ligand. Washing with hexanes removes excess ligand and leaves behind a solid mixture of **2** and **3**.

#### 2.2.4. Synthesis of $4 [P_4(NCH_3)_6](CuCl)_4$

Reactions with L:M ratios of 1:4 or lower yield the same compound. Cuprous chloride (0.183 mg, 1.85 mmol) was dissolved in 7 mL of dry acetonitrile. A solution of ligand in acetonitrile (0.132 g, 0.443 mmol) was added dropwise to the metal solution. A thick white precipitate formed immediately. After a few minutes, the thick precipitate became a free-flowing powder at the bottom of the flask. The reaction mixture was stirred for six days with no

Tal	ble	1			
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Crystallographic	details	for	structures	1	through 3.
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Compound	1	2	3
CSD# Formula Formula weight Space group a (Å) b (Å) c (Å) r ( $a$ )	743993 $C_{16}H_{42}Cl_3Cu_3N_{14}P_8$ 975.37 $P2_1/n$ 14.2863(5) 15.3649(5) 17.8721(6)	743994 $C_{12}H_{36}Cl_2Cu_2N_{12}P_8$ 794.27 $P\bar{1}$ 10.8351(4) 11.1744(4) 12.6817(4)	743995 C <sub>12</sub> H <sub>36</sub> ClCuN <sub>12</sub> P <sub>8</sub> 695.28 <i>Fdd</i> 2 14.7536 48.9841 7.9413
$ \begin{array}{l} \alpha \left( \circ \right) \\ \beta \left( \circ \right) \\ \gamma \left( \circ \right) \\ V \left( \dot{A}^{3} \right) \\ Z \end{array} $	90 111.478(2) 90 3650.6(2) 4	103.9222(19) 91.235(2) 102.718(2) 1449.27(9) 2	90 90 90 5739.11 8
ρ <sub>calc</sub> (g cm <sup>-3</sup> ) F(0 0 0) μ(Mo Kα) λ (Å)	1.775 1976 2.338 0.71073	1.820 808 2.124 0.71073	1.609 2864 1.329 0.71073
T (°C) R; wR Goodness-of-fit (GOF)	-173 0.0288; 0.0611 1.016	-173 0.0207; 0.0510 1.029	-173 0.0208; 0.0540 1.171

observable change. The solid product was filtered and washed with acetonitrile then dried briefly. Yield: 0.302 g (94%). Elemental *Anal.* Calc. for: C, 10.38; H, 2.61; N, 12.11; Cu, 36.61; P, 17.85. Found: C, 9.69; H, 2.81; N, 10.86; Cu, 36.0; P, 17.2%.

#### 2.2.5. Isolation of **5** and **6** from TGA residue

Samples of **1** were placed in a balance pan of the TGA and heated to 120 and 200 °C, respectively. Each sample was held at temperature for 10 min. The resulting powders were removed and subjected to elemental analysis. Some charring and copper metal was noted after 200 °C. Samples heated beyond 450 °C showed significant charring, decomposition, and the presence of copper metal in the pan.

# 2.3. X-ray crystallography

Crystals were handled under oil and the specimen crystals were affixed to the aperture of a MiTeGen MicroMount mounted to a tapered copper pin. This assembly was placed onto the goniometer of a Bruker KAPPA APEX II CCD diffractometer equipped with an Oxford Cryosystems Cryostream series 700 low-temperature apparatus operating at 100 K. The unit cell and orientation matrix were determined using reflections harvested from three sets of 12 0.5°  $\varphi$  scans, such that  $I > 2\sigma(I)$ . Final unit cell parameters were determined using reflections harvested from each entire data set. All data were corrected for Lorenz and polarization effects, as well as for absorption.

Structure solution and refinement utilized the SHELXTL Software package as implemented in the APEX2 software suite [42]. Figures were constructed and rendered using ORTEP-3 for Windows [43] and POV-RAY for Windows 3.6 [44]. A summary of crystallographic data for all compounds is provided in Table 1.

### 3. Results

# 3.1. Structures of 1, 2 and 3

#### 3.1.1. 3-D network

X-ray quality crystals of **1** grow from reaction mixtures containing a ligand-to-metal ratio of 2:1. A single crystal was chosen from the reaction mixture and mounted on a thin fiber. The structure of **1** is a three-dimensional array of formula  $[\mu_3-P_4(NCH_3)_6]_2(CuCl)_3$  CH<sub>3</sub>CNJ·CH<sub>3</sub>CN. The asymmetric unit of **1** is shown in Fig. 1, and exhibits the three different coordination environments for copper. Expansion of the structure about an inversion center generates the  $L_4Cu_4$  ring shown in Fig. 2. The tetrahedral coordination environment of Cu1 consists of P1 and P5 from different ligands and two symmetry equivalent Cl1 ions. Trigonal planar environment of



**Fig. 1.** Thermal ellipsoid plot of the asymmetric unit of **1**. Ellipsoids drawn at 50% probability. Hydrogen atoms and the unbound solvent molecule are removed for clarity.

Cu3 arises from coordination by P7 and P8 from different ligands and a terminal chloride, Cl3. Fig. 3 shows propagation of the  $L_4Cu_4$  ring structure along the *a*-axis, yielding a linear chain linked by shared Cu<sub>2</sub>Cl<sub>2</sub> dimers. The third environment for copper in **1** is tetrahedral, and consists of P3, P4 of an adjacent TPHMI, a terminal chloride, and N-bound acetonitrile. The result is Cu2 cross-linking the ( $L_4Cu_4$ )<sub> $\infty$ </sub> chains to form a three-dimensional network. A packing diagram, viewed down the *a*-axis of the unit cell, is shown in Fig. 4. The bond distances for copper atoms are typical for each of the three geometries observed.

The internal structure of the  $P_4N_6$  cage is distorted slightly from the ideal tetrahedral geometry. The P–N bonds range in length from 1.679(2) to 1.722(2) Å. Bonds that contain a P bound to Cu (e.g. P–N bonds to P1) are noticeably shorter (0.03 Å on average) than those where P does not interact with a metal. This shortening is compensated for by minor elongation of the adjacent N–P bonds (e.g. N1–P2). The sum of bond angles around N atoms in the cage varies from 357.9° to 343.5° and shows no correlation with the adjacent P atoms being bound to Cu.

#### 3.1.2. Ladder

Compound **2** crystallizes in the  $P\overline{1}$  space group, forming a ladder-type structure. A segment of the polymer is shown in Fig. 5. The Cu<sub>2</sub>Cl<sub>2</sub> dimers are linked by P atoms from TPHMI. The structure extends into polymer by coordination of a second P atom from a neighboring dimer. The packing diagram in Fig. 6 shows the parallel arrangement of polymer strands in the solid. Both copper atoms are tetrahedrally coordinated with Cu–Cl bond lengths in a narrow range of 2.3863(4)–2.4018(4) Å. The P–N bond lengths range in length from 1.6881(12) to 1.7230(12) Å, with the shortest distances where P is bound to Cu (0.02 Å shorter than average for other P–N bonds). The sum of the angle around N atoms in the cage range from 348.8° to 359.4° with no clear pattern related to bonding at adjacent P atoms.

#### 3.1.3. Monomer

Compound **3** crystallizes as a monomeric complex, shown in Fig. 7, in the orthorhombic space group *Fdd2*. The coordination geometry around Cu1 is planar with a P–Cu–P bond angle of 126.6° and a Cl–Cu–P, angle of 116.7°. The average P–N bond



**Fig. 2.** Structure of **1** expanded to show the Cu<sub>4</sub>L<sub>4</sub> ring and (CuCl)<sub>2</sub> dimer. Symmetry operations: (i) -x, -y, -z + 2; (ii) -x + 1, -y, -z + 2; (iii) x + 1/2, -y + 1/2, z + 1/2; (iv) x - 1/2, -y + 1/2, z - 1/2. Thermal ellipsoids drawn at 50% probability. Methyl groups are removed for clarity.



Fig. 3. The extended chain of L<sub>4</sub>Cu<sub>4</sub> rings along the *a*-axis. Thermal ellipsoids drawn at 50% probability. Methyl groups and solvent molecules removed for clarity.



Fig. 4. Partial packing diagram for 1 viewed down a-axis of the unit cell. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms removed for clarity.

lengths for P1 (bonded to Cu) are  $0.03^\circ \text{\AA}$  shorter than the average for adjacent P–N bonds. Of the three N atoms bound to P1, only

N3 has planar geometry. The P1–N3 bond is also the shortest of the three.



**Fig. 5.** A segment of coordination polymer compound **2**. Symmetry equivalent ligands generated by (i) -x + 1, y, -z + 1, (ii) -x + 2, -y + 1, -z + 1. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms removed for clarity.

Selected bond lengths and angles for all structures are presented in Table 2.

# 3.2. Thermogravimetric analysis of 1

Thermogravimetric traces for compounds **1**, **2** and **4** are shown in Fig. 8. When compound **1** is subjected to thermogravimetric analysis, the sample shows a mass loss event at 110 °C consistent with vaporization of the solvent molecules. The result is compound **5**, with the L:M ratio of 2:3. A second loss of mass is observed at 170 °C that is consistent with vaporization of 1/2 of one equivalent of ligand, resulting in compound **6** with L:M ratio of 1:2. Samples of both **5** and **6** were subjected to elemental analysis as support for the TGA results. The percent compositions were consistent, but not precise matches, to formulations of  $P_4(NCH_3)_6(CuCl)_3$  for **5** and  $P_4(NCH_3)_6(CuCl)_2$  for **6**. These results are collected in Table 3. X-ray powder diffraction measurements also suggest that little of **1** remains in the sample of **5**, and that **6** is free of contamination from **1** or **5**. Further heating causes a rapid loss of mass at 280 °C, resulting in decomposition.

Mass losses for compounds **2** and **4** are less well defined. Compound **2** undergoes a 20% mass loss at 180 °C, consistent with the loss of one quarter of the ligand from the sample. No further analysis of TGA data was attempted.

# 4. Discussion

TPHMI reacts with cuprous chloride in acetonitrile to form a series of compounds. Depending on the stoichiometry of the reaction mixture, products with ligand-to-metal (L:M) ratios ranging from 1:4 to 2:1 have been observed. An equimolar reaction of ligand and metal yields a solvated product with a 2:3:2 (L:M:solvent) ratio **1**. With L:M > 3 the "ladder-type" coordination

polymer **2**, precipitates. Higher L:M ratios result in a mixture of products containing **2** and the monomeric compound **3**. Reactions of  $P_4(NCH_3)_6$  with CuCl in ratios less than 1 seem to yield a smaller range of products. Reactions with L:M ratios between 0.5 and 1 yield impure samples of **1**. Reactions where L:M is less than 0.25 all yield the same compound, **4**, tentatively assigned the formula  $P_4(NCH_3)_6(CuCl)_4$ . Attempts to grow X-ray quality crystals of **4** have been unsuccessful to date.

Structural characterization of **1–3** show that they are typical examples of both the coordination chemistry of copper chloride and the internal bonding of the  $P_4(NCH_3)_6$  ligand system. The P–N bond lengths of  $P_4(NCH_3)_6$  are variable, and influenced by crystal packing forces, and the other atoms bonded to P [37,45]. In this series of compounds, P–N bond lengths in the cage range as much as 0.04 Å, depending on proximity to a P–Cu bond. These effects are small when compared to those observed for the chalcogen derivatives [45–47] or the methylphosphonium  $P_4(NCH_3)_6CH_3I$  structure [48].

It is interesting to note that in all reactions where  $L:M \ge 1$  there is instantaneous formation of an amorphous precipitate that disappears with stirring. In reactions where L:M < 1, the immediate product does not redissolve, but the consistency changes from globular to free-flowing powder over several minutes. Observation of this type of "kinetic product" has been noted previously in similar nitrogen bridged systems [49].

Isolation of multiple products from Cu(I)–phosphine systems based on different L:M ratios is well-documented in the literature [50,51]. Studies of the solution phase equilibria for copper halide complexes of tertiary phosphines (Ph<sub>3</sub>P and Ph<sub>2</sub>MeP) have shown that L<sub>2</sub>CuCl is the dominant species in solution when L:M > 3, and that multiple equilibria for ligand dissociation and halide bridging give rise to a wide variety of species in solution [52]. Multiple equilibria are also observed in the reaction of P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub> with



Fig. 6. Partial packing diagram for 2 viewed parallel to the polymer chains. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms removed for clarity.



Fig. 7. Thermal ellipsoid plot of 3 drawn at 50% probability. Symmetry equivalent ligand generated by (i) – x + 3/2, –y + 1/2, z. Hydrogen atoms removed for clarity.

Lewis acids, where intermediates can be observed by <sup>31</sup>P NMR [39,40,53,54]. In the case of **1**, it appears that the multiple solution equilibria and the low solubility of the coordination network lead

to a product that displays multiple coordination environments for copper. Attempts to study the  $P_4(NCH_3)_6/CuCl$  equilibria by solution NMR are complicated by precipitation of the products,

Table 2				
Selected bond lengths	and angles	for 1	through	3

1		2		3	
Cu1-P1	2.2570(7)	Cu1-P1	2.2754(4)	Cu1-P1	2.2187(4)
Cu1-P5	2.2598(7)	Cu1-P7(ii)	2.2764(4)	Cu1-Cl1	2.2060(7)
Cu1–Cl1	2.4017(7)	Cu1–Cl1	2.4018(4)		
Cu1-Cl1(i)	2.4203(7)	Cu1-Cl2	2.3863(4)		
Cu2-N13	2.042(2)	Cu2-P5	2.2756(4)		
Cu2-P3	2.2364(7)	Cu2-P3(ii)	2.2780(4)		
Cu2–P4	2.2422(7)	Cu2–Cl1	2.3995(4)		
Cu2-Cl2	2.3015(7)	Cu2–Cl2	2.3983(4)		
Cu3–Cl3	2.2032(8)				
Cu3–P8	2.2036(7)				
Cu3–P7	2.2278(7)				
P1-Cu1-P5	121.03(3)	P1-Cu1-P7(i)	117.381(14)	Cl1-Cu1-P1	116.708(11)
P1-Cu1-Cl1	105.03(3)	P1-Cu1-Cl2	107.812(13)	P1-Cu1-P1(i)	126.58(2)
P5-Cu1-Cl1	114.32(3)	P7(i)-Cu1-Cl2	117.425(13)		
P1-Cu1-Cl1(ii)	112.53(3)	P1-Cu1-Cl1	112.870(13)		
P5-Cu1-Cl1(ii)	110.40(3)	P7(i)-Cu1-Cl1	109.054(13)		
Cl1-Cu1-Cl1(ii)	88.89(2)	Cl2-Cu1-Cl1	88.906(12)		
N13-Cu2-P3	104.14(7)	P5-Cu2-P3(ii)	117.319(14)		
N13-Cu2-P4(iv)	102.32(7)	P5-Cu2-Cl2	108.349(13)		
P3-Cu2-P4(iv)	133.57(3)	P3(ii)-Cu2-Cl2	115.807(14)		
N13-Cu2-Cl2	108.78(7)	P5-Cu2-Cl1	114.771(13)		
P3-Cu2-Cl2	100.38(3)	P3(ii)-Cu2-Cl1	108.584(13)		
P4(iv)-Cu2-Cl2	106.24(3)	Cl2-Cu2-Cl1	88.680(12)		
Cl3-Cu3-P8	116.87(3)	Cu2–Cl1–Cu1	90.993(12)		
Cl3-Cu3-P7(i)	117.56(3)	Cu1-Cl2-Cu2	91.399(12)		
P8-Cu3-P7(i)	125.36(3)				
Cu1–Cl1–Cu1(ii)	91.11(2)				

Thermogravimetric traces for compounds 1, 2 and 4



Fig. 8. Thermogravimetric traces for compounds 1, 2 and 4.

Thermogravimetric	analysis	of [P <sub>4</sub> (NC	Ha)ala(CuC	1) <sub>2</sub> CH <sub>2</sub> CN <sub>2</sub> C	$H_{2}CN(1)$

Table 3

Temperature	Resulting	Analysis %C, %H,	Theory %C, %H, %N,
(mass loss) °C (%)	material	%N, %P, %Cu	%P, %Cu
110 (9.2)	(L) <sub>2</sub> (CuCl) <sub>3</sub>	16.46, 3.69,	16.13, 4.06, 18.82,
	compound <b>5</b>	18.55, 26.9, 20.4	27.74, 21.34
171 (15.5)	(L)(CuCl) <sub>2</sub>	14.34, 3.30,	14.52, 3.66, 16.94,
	compound <b>6</b>	16.10, 23.7, 23.9	24.97, 25.61

and the quadrupolar moment of Cu. Studies of cuprous ions coordinated to modified cage ligands  $P_4(NR)_6$  where R = ethyl and *n*-propyl) and the use of non-bridging anions like  $PF_6^-$  are underway.

Elemental analysis of compounds presented in this work provides only approximate matches for many of the compounds. The likely presence of multiple equilibria in solution and the observed co-precipitation of multiple products from reaction mixtures suggest that any bulk sample isolated from this reaction system is likely to contain impurities of the other phases. This problem is illustrated by the isolation of mixtures of **2** and **3** during attempts to collect pure bulk samples of **3**. A similar mixture of **1** and **4** is isolated when a L:M reaction ratio of 1:2 is employed in attempted preparation of (TPHMI)(CuCl)<sub>2</sub>. The presence of a small amount of **3** in samples of compound **2** could explain the poor results for phosphorus analysis. Decomposition during thermal analysis of **1** produced some copper metal, which was not included in samples of **5** and **6** submitted for analysis. These products were recovered under aerobic conditions, providing a possibility of further decomposition during sample transfer.

Thermogravimetric analysis of **1** displays aspects similar to Nbridged networks of copper halides [49]. Solvent molecules are lost at relatively low-temperatures with subsequent loss of ligand to yield materials of new composition. Heating a sample of **1** provides a route to isolating compounds **5** and **6** that were otherwise not isolated from solution reactions. This is particularly interesting in the case of **6**, since solution reactions of L:M = 0.5 do not produce  $L(CuCl)_2$ , but do yield impure **1** mixed with **4**.

To our knowledge, there are currently no structural examples of HMTA/CuCl based coordination polymers to compare with the  $P_4(NCH_3)_6/CuCl$  system. But a similar variety of coordination modes is found in a number of HMTA-containing systems when paired with silver ions [33,55]. The one structure found for the analogous HMTA/AgCl series displays three different coordination environments for the metal [56]. So far, reactions of  $P_4(NCH_3)_6$  with silver salts have resulted only in reduction of the Ag(I) to silver metal.

### 5. Conclusion

The tetradentate ligand  $P_4(NCH_3)_6$  forms at least four coordination compounds with cuprous chloride in acetonitrile at room temperature and atmospheric pressure. The composition of these products ranges in ligand-to-metal ratio from 1:4 to 2:1. Structurally characterized forms include a monomeric compound, a polymeric ladder structure, and a three-dimensional structure of cross-linked chains. These observations show that  $P_4(NCH_3)_6$  has the potential to be a useful building block for the synthesis of phosphorus(III)-bridged MOFs. Changes to solvent system, temperature and pressure are currently under investigation in attempts to observe more phases of the P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub>/CuCl. Still more variations of the networks formed by this ligand are possible through addition of auxiliary ligands to the metal center and use of other counterions for Cu(I).

# 6. Supplementary data

CCDC 743993, 743994 and 743995 contain the supplementary crystallographic data for compounds 1, 2 and 3. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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#### References

- [1] C.A. Bayse, T.P. Brewster, R.D. Pike, Inorg. Chem. 48 (2009) 174.
- [2] M. Dinca, J.R. Long, Angew. Chem., Int. Ed. 47 (2008) 6766.
- [3] S. Horike, M. Dinca, K. Tamaki, J.R. Long, J. Am. Chem. Soc. 130 (2008) 5854.
- [4] S.S. Kaye, J.R. Long, J. Am. Chem. Soc. 130 (2008) 806.
- [5] M.J. Lim, C.A. Murray, T.A. Tronic, K.E. deKrafft, A.N. Ley, J.C. deButts, R.D. Pike, H. Lu, H.H. Patterson, Inorg. Chem. 47 (2008) 6931.
- [6] J.L.C. Rowsell, O.M. Yaghi, Angew. Chem., Int. Ed. 44 (2005) 4670.
- [7] T.A. Tronic, K.E. De Krafft, M.J. Lim, A.N. Ley, R.D. Pike, Inorg. Chem. 46 (2007) 8897
- [8] M.-C. Brandys, R.J. Puddephatt, J. Am. Chem. Soc. 124 (2002) 3946.
- [9] T.J. Burchell, D.J. Eisler, M.C. Jennings, R.J. Puddephatt, Chem. Commun. (2003) 2228
- [10] R.P. Feazell, C.E. Carson, K.K. Klausmeyer, Inorg. Chem. 44 (2005) 996.
- [11] F. Hung-Low, K.K. Klausmeyer, J.B. Gary, Inorg. Chim. Acta 362 (2009) 426.
- [12] W.J. Hunks, M.C. Jennings, R.J. Puddephatt, Chem. Commun. (2002) 1834.
- [13] S.L. James, X. Xu, R.V. Law, Macromol. Symp. 196 (2003) 187
- [14] S.L. James, X. Xu, M. Nieuwenhuyzen, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 45 (2004) 423.

- [15] K.K. Klausmeyer, R.P. Feazell, J.H. Reibenspies, Inorg. Chem. 43 (2004) 1130.
- [16] H. Krishna, S.S. Krishnamurthy, Inorg. Chim. Acta 360 (2007) 3462.
- [17] E. Lozano, M. Nieuwenhuyzen, S.L. James, Chem.-Eur. J. 7 (2001) 2644.
- [18] P.W. Miller, M. Nieuwenhuyzen, J.P.H. Charmant, S.L. James, Inorg. Chem. 47 (2008) 8367.
- [19] J.M.J. Paulusse, J.P.J. Huijbers, R.P. Sijbesma, Macromolecules 38 (2005) 6290.
- [20] Z. Qin, M.C. Jennings, R.J. Puddephatt, Chem.-Eur. J. 8 (2002) 735.
- [21] X. Xu, E.J. MacLean, S.J. Teat, M. Nieuwenhuyzen, M. Chambers, S.L. James, Chem. Commun. (2002) 78.
- [22] X. Xu, M. Nieuwenhuyzen, S.L. James, Angew. Chem., Int. Ed. 41 (2002) 764. [23] X. Xu, J. Zhang, A. Pichon, A.L. Garay, S.L. James, Polym. Prepr. (Am. Chem. Soc.,
- Div. Polym. Chem.) 48 (2007) 566.
- [24] J. Bai, A.V. Virovets, M. Scheer, Angew. Chem., Int. Ed. 41 (2002) 1737.
- [25] P.D. Harvey, in: A.S. Abd-El-Aziz, I. Manners (Eds.), Frontiers in Transition Metal-Containing Polymers, John Wiley and Sons, Hoboken, NJ, 2007, p. 321. [26] D. Samar, J.-F. Fortin, D. Fortin, A. Decken, P.D. Harvey, J. Inorg. Organomet.
- Polym. Mater. 15 (2006) 411.
- [27] P.D. Harvey, E. Fournier, ACS Symp. Ser. 928 (2006) 472.
- [28] E. Fournier, S. Sicard, A. Decken, P.D. Harvey, Inorg. Chem. 43 (2004) 1491.
- [29] P.D. Harvey, Macromol. Symp. 196 (2003) 173.
- [30] M.A. Fox, D.A. Chandler, Adv. Mater. (Weinheim, Ger.) 3 (1991) 381.
- [31] R.D. Pike, B.A. Reinecke, M.E. Dellinger, A.B. Wiles, J.D. Harper, J.R. Cole, K.A. Dendramis, B.D. Borne, J.L. Harris, W.T. Pennington, Organometallics 23 (2004) 1986.
- [32] C. Sivasankar, M. Nethaji, A.G. Samuelson, Inorg. Chem. Commun. 7 (2004) 238.
- [33] S.-L. Zheng, M.-L. Tong, X.-M. Chen, Coord. Chem. Rev. 246 (2003) 185.
- R.D. Sommer, A.L. Rheingold, Acta Crystallogr., Sect. E: Struct. Rep. Online E62 Ì34Ì (2006) m74.
- [35] R.R. Holmes, J. Am. Chem. Soc. 83 (1961) 1334.
- [36] R.R. Holmes, J.A. Forstner, Inorg. Synth. 8 (1966) 63.
- [37] F.A. Cotton, J.G. Riess, B.R. Stults, Inorg. Chem. 22 (1983) 133.
- [38] J. Reiss, J.R.V. Wazer, Bull. Soc. Chim. Fr. (1966) 1846.
- [39] J.G. Riess, J.R. Van Wazer, J. Organomet. Chem. 8 (1967) 347.
- [40] J.G. Riess, J.R. Van Wazer, Bull. Soc. Chim. Fr. (1968) 3087.
- [41] R.W.L. Kimber, I.F. Fergus, Fert. Res. 5 (1984) 245.
- [42] Bruker AXS Inc., Madison, WI 53719, USA, 2004.
- [43] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
- [44] Persistence of Vision Raytracer, Version 3.6, Retrieved from: <a href="http://">http://</a> www.povray.org/download/>, 2004.
- [45] F. Casabianca, F.A. Cotton, J.G. Riess, C.E. Rice, B.R. Stults, Inorg. Chem. 17 (1978) 3232.
- [46] F.A. Cotton, J.G. Riess, C.E. Rice, B.R. Stults, Inorg. Chem. 21 (1982) 3123.
- A. Wolff, J.G. Riess, Bull. Soc. Chim. Fr. (1973) 1587. [47]
- [48] G.W. Hunt, A.W. Cordes, Inorg. Chem. 13 (1974) 1688.
- [49] P.M. Graham, R.D. Pike, M. Sabat, R.D. Bailey, W.T. Pennington, Inorg. Chem. 39 (2000) 5121.
- [50] J.T. Gill, J.J. Mayerle, P.S. Welcker, D.F. Lewis, D.A. Ucko, D.J. Barton, D. Stowens, S.J. Lippard, Inorg. Chem. 15 (1976) 1155.
- S.J. Lippard, J.J. Mayerle, Inorg. Chem. 11 (1972) 753. [51]
- [52] D.J. Fife, W.M. Moore, K.W. Morse, Inorg. Chem. 23 (1984) 1684.
- [53] J.C. Elkaim, A. Wolff, J.G. Riess, Phosphorus Relat. Group V Elem. 2 (1973) 249.
- [54] J.G. Riess, A. Wolff, Chem. Commun. (1972) 1050.
- [55] V.V. Kinzhibalo, M.G. Mys'kiv, V.N. Davydov, Russ. J. Coord. Chem. 28 (2002) 867
- [56] T.C.W. Mak, Inorg. Chim. Acta 84 (1984) 19.