

## Novel Layered Copper Phosphoramidate, Which Contains Six-Membered Rings Made of Five Different Elements

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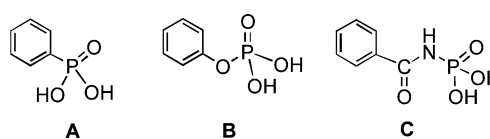
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Copper(II) perchlorate and  $(\text{PhCONH})\text{P}(\text{O})(\text{OH})_2$  ( $\text{H}_2\text{bpa}$ ) react in methanol to yield  $[\text{Cu}(\text{Hbpa})_2]_n$ , a novel layered solid that displays several interesting features. Unlike the previously reported copper phosphonates, a rare hexacoordination around the metal is observed in the title compound because of the amide  $\text{C}=\text{O}$  coordination to Cu in addition to the phosphoramidate  $\text{P}-\text{O}$  coordination. The six-membered chelate rings present in the title compound are made up of five different elements (Cu, P, C, N, and O).

The chemistry of metal phosphonates,  $[\text{RPO}_3\text{M}]$ , has been a well-investigated area since the 1970s because of application of these layered compounds in ion-exchange, catalysis, chemical-sensing, and electrooptics processes.<sup>1</sup> The structure and properties of these hybrid materials, which integrate organic and inorganic characteristics within a single extended framework, can often be modified by incorporation of additional functions such as hydroxy, amino, carboxylate, and pyridyl in the R group.<sup>2</sup> While most of these functional groups are appended to the 4 position of the phenyl group of an arylphosphonic acid (**A**)<sup>3</sup> or at the end of an alkyl substituent, e.g.,  $\text{CH}_2\text{CH}_2\text{NH}_2$  or  $\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$ ,<sup>4</sup> introduction of functionalities between P and the phenyl ring or the aliphatic C is largely unknown, except the case of  $[(\text{PhO})\text{PO}_3\text{H}_2]$  (**B**). In case of **B**, the extra O significantly modifies the overall reactivity but does not contribute to additional bonding interactions.<sup>5</sup> In contrast, *N*-benzoylphosphoramidic acid ( $\text{H}_2\text{bpa}$ , **C**) is a molecule that not only has

structural similarities to **A** and **B** but also incorporates additional functions between P and the phenyl ring.



Although  $\text{H}_2\text{bpa}$  (**C**) has been known in the literature for almost a century now,<sup>6</sup> its preparation (in the free acid form) and characterization have been nontrivial, which appears to be the reason for the absence of any attempts to study its ligation capabilities. This is surprising because of the fact that, apart from possessing the usual  $-\text{PO}_3\text{H}_2$  functionality,  $\text{H}_2\text{bpa}$  also integrates an  $\text{C}(=\text{O})\text{NH}$  linkage that could further stabilize the resultant complex either by additional coordination to the metal or by hydrogen-bonding interactions.

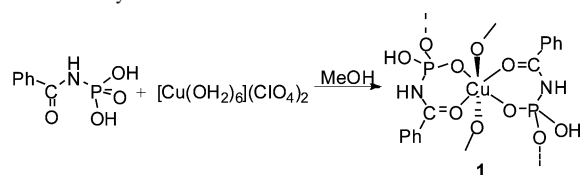
Continuing our studies on metal phosphates,<sup>7</sup> in order to exploit the utility of  $\text{H}_2\text{bpa}$  in the synthesis of new layered solids, we have investigated its reaction chemistry with Cu salts in the present study. Thus, the reaction of copper(II) perchlorate with  $\text{H}_2\text{bpa}$  in a 1:1 molar ratio in methanol proceeds smoothly within 2 h and produces  $[\text{Cu}(\text{Hbpa})_2]$  (**1**) as a pale-blue precipitate. Removal of this precipitate by filtration followed by leaving the clear dilute filtrate for crystallization produces X-ray diffraction quality single crystals of **1** (Scheme 1).<sup>8</sup>

Compound **1** is characterized by elemental analysis, thermal analysis [thermogravimetric analysis/differential scanning calorimetry (TGA/DSC)], spectroscopy [IR and electron paramagnetic resonance (EPR)], and X-ray diffraction (powder and single crystal). The crystallized sample of **1** is insoluble in water, methanol, and other common organic

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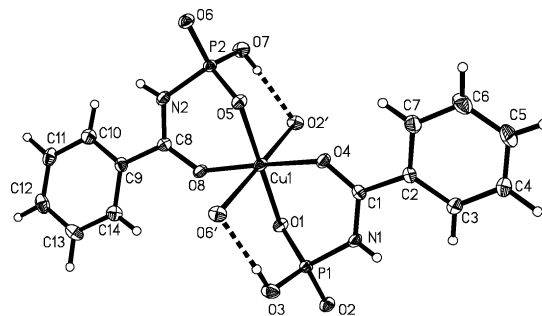
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Scheme 1. Synthesis of **1**

solvents, although the compound melts at 215–220 °C. The elemental analysis values suggest that the metal is surrounded by just two Hbpa<sup>−</sup> anions and no other additional ligands (such as water). IR spectroscopy confirms the absence of coordinated or lattice water in the complex. The characteristic absorptions at 3318 (sharp) and 1608 cm<sup>−1</sup> confirm that the N–H and C=O groups of the ligand are intact in the complex. The presence of absorption at 2332 cm<sup>−1</sup> due to the free O–H group (on P) indicates that the H<sub>2</sub>bpa ligand is not completely deprotonated in **1**. Three lines corresponding to all three *g* components are observed (*g*<sub>1</sub> = 2.2; *g*<sub>2</sub> = 2.1; *g*<sub>3</sub> = 2.0) in the EPR spectrum of crystalline **1** recorded at both 298 and 77 K.

To unambiguously establish the mode of binding of Hbpa<sup>−</sup> to Cu and also to unravel the role played by C=O and N–H groups, a single-crystal X-ray diffraction study was carried out.<sup>9</sup> The powder X-ray diffraction of the bulk sample of **1** matches with the simulated diffraction pattern from the single-crystal diffraction data. The repeating unit, which represents the asymmetric part of the unit cell, is shown in Figure 1. The Cu ion in **1** is hexacoordinated, unlike the previously reported layered copper phosphonates [Cu(O<sub>3</sub>PR)(OH<sub>2</sub>)] (R = methyl, ethyl, allyl, and phenyl), which contain pentacoordinated Cu.<sup>10–12</sup> In fact, the layered copper phosphonates formed by 1,4-phenylenebis(phosphonic acid) and 1,3,5-benzenetriphosphonic acid also contain pentacoordinated Cu in a square-pyramidal coordination environment.<sup>13</sup>



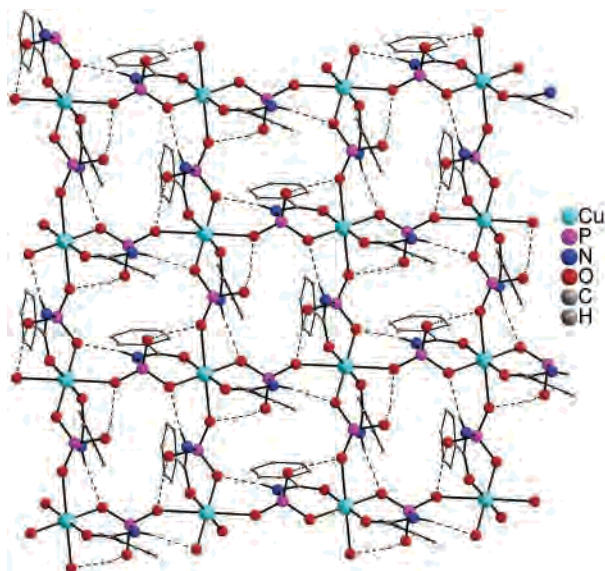
**Figure 1.** ORTEP representation of the repeating unit in **1**. Selected bond distances [Å] and angles [deg]: Cu1–O1 1.934(1), Cu1–O5 1.927(1), Cu1–O4 1.965(1), Cu1–O8 1.962(1), Cu1–O2' 2.458(8), Cu1–O6' 2.546(9), P1–O1 1.503(1), P1–O2 1.484(1), P1–O3 1.560(1), P1–N1 1.697(2), P2–O5 1.506(1), P2–O6 1.482(1), P2–O7 1.557(2), P2–N2 1.702(2), C1–O4 1.248(2), C8–O8 1.248(2); O1–Cu1–O5 179.91(6), O4–Cu1–O8 1771.6(6), O2'–Cu1–O6' 178.37(1), O5–Cu1–O8 92.48(5), O1–Cu1–O8 87.46(5), O4–Cu1–O5 88.44(5), O1–Cu1–O4 91.61(5).

The six Cu–O bonds around Cu in **1** fall into two categories. The four short Cu–O bonds arise from the chelation by two [PhCONHP(O)(OH)O]<sup>−</sup> ligands, which bind the metal through the phosphoryl O<sup>−</sup> oxygen as well as the C=O group. The resultant Cu–O–P–N–C–O six-membered rings contain five different elements (Cu, P, N, C, and O), which is uncommon in inorganic ring systems. The bis-chelation of Hbpa in **1** has a similarity to the binding of  $\beta$ -diketonate ligands to Cu in complexes that display square-planar geometry.<sup>14</sup> The two longer Cu–O bonds [Cu1–O2' 2.458(8) Å; Cu1–O6' 2.546(9) Å] on the axial sites, which complete the octahedral geometry around Cu in **1**, originate from the phosphoryl group of the adjacent Cu(Hbpa)<sub>2</sub> units. Thus, each H<sub>2</sub>bpa ligand functions as a chelating bidentate ligand to the first Cu and as a monodentate bridging ligand to the second Cu, which, in turn, is responsible for the formation of tetrameric building blocks. These tetrameric blocks are tiled in the *ab* plane to result in a two-dimensional sheet.

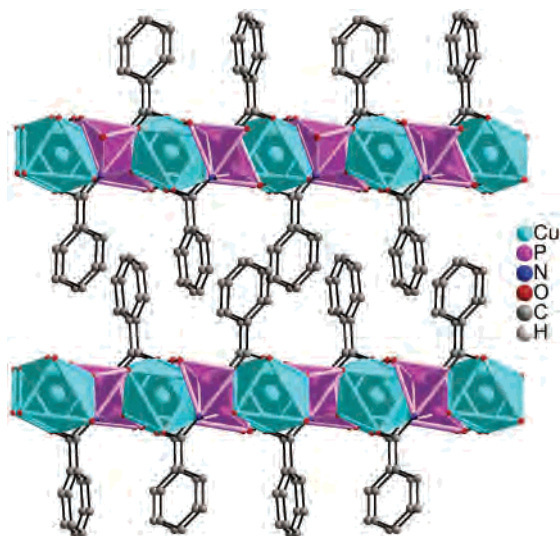
The two-dimensional sheets shown in Figure 2 stack along the *c* axis (one over another in a staggered fashion) to produce a layered structure that is shown in Figure 3. Unlike in the previously described layered metal phosphonates formed by phenylphosphonic acid where only weak van der Waals interactions were found between the layers,<sup>10a,15</sup> a  $\pi$ – $\pi$  stacking of phenyl rings from adjacent layers is observed in **1**. Because of this, the interlayer distance in **1** is only 10.46 Å (half of the length of the *c* axis), although the thickness of each layer is 15.51 Å. In contrast, the layer thickness as well as the interlayer distance in the case of [Cu(PhPO<sub>3</sub>)(H<sub>2</sub>O)] is 14.0 Å, where no  $\pi$ – $\pi$  stacking of phenyl rings from the adjacent layers is observed.<sup>10a</sup> The  $\pi$ – $\pi$  stacking of phenyl rings in the case of **1** has been made possible

- (8) To a stirred solution of H<sub>2</sub>bpa (0.201 g, 1.0 mmol) in methyl alcohol (30 mL) was added hexa-aquacopper(II) perchlorate (0.370 g, 1.0 mmol) in one shot, and the resulting light-blue solution was stirred at room temperature for 2 h, during which time a blue precipitate of **1** is formed. The reaction mixture was filtered, and the clear blue solution was kept at room temperature for crystallization. Blue crystals of [Cu(Hbpa)<sub>2</sub>]<sub>n</sub> X-ray diffraction quality appeared after 2 days. Combined yield of precipitate and crystals: 90%. Mp: 215–220 °C. Anal. Calcd for C<sub>14</sub>H<sub>14</sub>CuN<sub>2</sub>O<sub>8</sub>P<sub>2</sub> (MW: 463.75): C, 36.26; H, 3.04; N, 6.04. Found: C, 35.62; H, 2.89; N, 6.58. IR (KBr, cm<sup>−1</sup>): 3318(s), 2332(m), 1608(s), 1571(s), 1509(s), 1478(s), 1300(s), 1184(s), 1068(s), 953(s), 710(w), 504(w).  $\mu_{298K}$  = 1.84  $\mu_B$ . EPR: average *g* factor = 2.1, *g*<sub>1</sub> = 2.2, *g*<sub>2</sub> = 2.1, *g*<sub>3</sub> = 2.0.
- (9) Crystal data for [Cu(Hbpa)<sub>2</sub>]: C<sub>14</sub>H<sub>14</sub>CuN<sub>2</sub>O<sub>8</sub>P<sub>2</sub>, monoclinic, space group *P2<sub>1</sub>/n*, *a* = 9.296(2) Å, *b* = 8.905(2) Å, *c* = 21.031(3) Å,  $\beta$  = 92.14(1)°, *V* = 1739.8(5) Å<sup>3</sup>, *Z* = 4, *d<sub>c</sub>* = 1.770 mg m<sup>−3</sup>,  $\lambda$  = 0.710 73 Å,  $\mu$  = 1.487 mm<sup>−1</sup>, 16 796 reflections, 5671 unique (*R<sub>int</sub>* = 0.0303), *R*<sub>1</sub> = 0.0324, *wR*<sub>2</sub> = 0.0787 [*I* > 2 $\sigma$ (*I*)].
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**Figure 2.** Two-dimensional sheet structure formed by a bridging Hbpa ligand as viewed down the *c* axis. The H atoms are omitted for clarity.



**Figure 3.** Section of the layered structure of **1** viewed down the *b* axis. The H atoms are omitted for clarity.

because of the less density of phenyl rings on each side of the layer, which, in turn, arises because of the presence of a CONH spacer between the phenyl ring and P. This is also reflected in the large Cu $\cdots$ Cu separations (6.401 and 6.475 Å) in the two-dimensional sheet shown in Figure 3, whereas smaller metal–metal separations are observed in [Cu-(PhPO<sub>3</sub>)(H<sub>2</sub>O)].<sup>10a</sup> Thus, the presence of the amide linkage not only aids additional coordination to the metal but also increases the intermetal distances and, hence, favors  $\pi$ – $\pi$

stacking. The presence of free P–OH and N–H groups in the layers results in hydrogen-bonding interactions (details in the Supporting Information), which along with  $\pi$ – $\pi$  stacking renders the layers more compact and, hence, results in a large crystal density.

TGA of **1** reveals no weight loss up to 200 °C due to the absence of any coordinated or lattice water in the compound. A total of 2 equiv of benzamide is lost in the temperature range 200–400 °C to yield the metaphosphate Cu(PO<sub>3</sub>)<sub>2</sub>, which remains stable at least until 800 °C. After this temperature, another weight loss is observed presumably because of the loss of P<sub>2</sub>O<sub>5</sub> to form pyrophosphate. It is interesting to note that the first weight loss onsets almost near the melting point of **1**. The powder X-ray diffraction pattern of the pyrolyzed sample at 600 °C matches well with that of Cu(PO<sub>3</sub>)<sub>2</sub>, further supporting the TGA studies.

The magnetic susceptibility data at 25 °C yield the magnetic moment of 1.84  $\mu_B$ , which is close to the spin-only magnetic moment value; no apparent magnetic coupling is observed between the Cu ions once again because of the large metal–metal distances.

In summary, we have presented a new type of a metal–phosphorus acid based layered solid involving *N*-benzoylphosphoramidic acid. The presence of a CONH group between P and the aryl ring facilitates the formation of hexacoordinated Cu ions unlike the pentacoordination observed for Cu in methyl and phenyl phosphonates. The amide linkage is also responsible for several structural peculiarities in **1** compared to the parent phosphonates including short interlayer spacing. It would be interesting to investigate the strength of the longer Cu–O bonds in **1** through intercalation studies involving long alkyl chain amines and also to explore the possibility of breaking the  $\pi$ – $\pi$  interactions and increasing the interlayer distances. The use of other metal ions and different stoichiometries of H<sub>2</sub>bpa could lead to other interesting possibilities. We are currently investigating these aspects.

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**Supporting Information Available:** Details of X-ray diffraction studies (CIF) and synthesis of H<sub>2</sub>bpa and characterization data for **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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