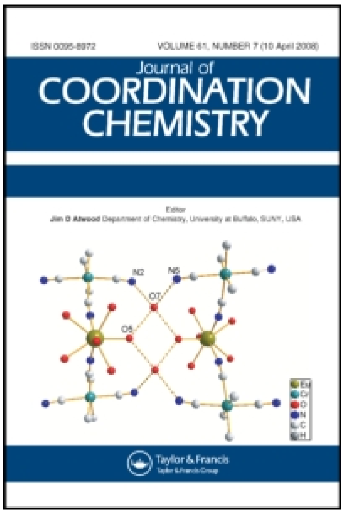

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Hydrothermal synthesis, structures and characterization of two new copper(II) triphosphonate compounds

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Hydrothermal synthesis, structures and characterization of two new copper(II) triphosphonate compounds

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Two copper(II) triphosphonate compounds, $Cu[(APTPH_4)(phen)(H_2O)]\cdot 2.16H_2O$ (**1**) and $[Cu(APTPH_4)(2,2'\text{-bipy})(H_2O)]\cdot 2.63H_2O$ (**2**), have been prepared by a low temperature hydrothermal reaction from 1-aminopropane-1,1,3-triphosphonic acid ($APTPH_6$), CuO and a second ligand, phen = 1,10-phenanthroline, or 2,2′-bipy = 2,2′-bipyridyl. These two compounds were characterized by single crystal X-ray diffraction, elemental analysis, IR and TG. Crystal data for **1**: *Monoclinic*, space group $P2_1/c$, $a = 14.4830(7)$ Å, $b = 9.1721(5)$ Å, $c = 16.7403(8)$ Å, $\beta = 90.101(2)°$. For compound **2**: *Triclinic*, space group $P\bar{1}$, $a = 7.1215(7)$ Å, $b = 10.460(2)$ Å, $c = 14.671(2)$ Å, $\alpha = 82.983(2)°$, $\beta = 83.882(2)°$, $\gamma = 80.617(2)°$. In both compounds, each Cu^{2+} ion is five-coordinate with two oxygen atoms from the triphosphonate, two nitrogen atoms from the second ligand and one water molecule, to form a distorted square-pyramidal geometry. Both complexes have 3D supramolecular structures constructed by hydrogen bonds and π–π stacking interactions.

Keywords: Triphosphonate; Copper; Supramolecular; Crystal structure

1. Introduction

Metal organophosphonate compounds are an important class of inorganic-organic hydrid materials, widely investigated in recent years due to their potential applications in molecular recognition, selective absorption, sensors, and so forth [1–3]. Among the diverse phosphonic acids, current interests focus on monophosphonic acids and diphosphonic acids [4–9]. More recently, *Zheng* and her coworkers [10] have investigated 1-hydroxyethylidenediphosphonic acid. The structures of its compounds range from one-dimensional chains, two-dimensional layers to three-dimensional pillared layers or open frameworks. *Clearfield* and coworkers reported on amino-diphosphonic acids coordinated with a variety of metal ions, including divalent and trivalent group 4 and 14 ions, giving layered species in which the metal octahedra are bridged by phosphonate tetrahedra to form two-dimensional layers [11]. Compounds based on triphosphonic acids have received little attention. Compared to diphosphonic acids, they are multidentate ligands with three phosphonate groups, which can complex

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metal ions in several ways by loss of one or more protons. In addition, their complexing ability can be modified by selection of the organic functional groups [3]. A tridentate ligand, 1-aminopropane-1,1,3-triphosphonic acid ($APTPH_6$), has been synthesized [12]. As far as we are aware, no examples of metal-APTP compounds have been structurally characterized. In this paper, two compounds of 1-aminopropane-1,1,3-triphosphonic acid: $Cu[(APTPH_4)(phen)(H_2O)] \cdot 2.16H_2O$ (**1**) and $[Cu(APTPH_4)(2,2'\text{-bipy})(H_2O)] \cdot 2.63H_2O$ (**2**) in which hydrogen bonds and π–π stacking interactions are predominant resulting in three-dimensional (3D) supramolecular structures are synthesized. Their structural characterizations, thermal stability and magnetic properties were also investigated.

2. Experimental

2.1. *Materials and methods*

The 1-aminopropane-1,1,3-triphosphonic acid ($APTPH_6$) was prepared according to the US Patent. The other starting materials were purchased from commercial sources and used without further purification. The IR spectra were recorded from KBr pellets in the range 400–4000 cm^{-1} on a Nicolet 5700 FT-IR spectrometer with spectral resolution of 4.00 cm^{-1}. Thermogravimetric studies were carried out with a NETZSCH STA 449C at a heating rate of 20 $K\,min^{-1}$ under air. The elemental analysis data were obtained from a Perkin–Elmer 240B elemental analyzer. Magnetic properties were investigated by a PPMS-9T magnetometer at a field of 5000 Oe in the temperature range of 2–300 K. These two compounds have similar structures, both illustrate 3D supramolecular structures constructed by hydrogen bonds and π–π interactions, so only the magnetic property of compound **1** was measured. From the experiment, we found a weak ferromagnetic interaction for Cu(II) (See S-1 in supporting information).

2.2. *Synthesis of $Cu[(APTPH_4)(phen)(H_2O)] \cdot 2.16H_2O$ (1)*

In a typical synthesis, 0.1495 g (0.5 mmol) $APTPH_6$ with 0.0199 g (0.25 mmol) CuO and 0.0496 g phen (0.25 mmol) in 0.8 mL deionized distilled water was transferred into a Teflon-lined stainless steel vessel that was heated at 80°C for 4 days. Blue crystals were filtered, washed with distilled water, and air dried (yield: 70.0% based on CuO). Anal. Calcd for **1**: C, 30.0; H, 4.1; N, 7.0; Found: C, 30.1; H, 4.1; N,7.1; Main IR bands (KBr, cm^{-1}): 3423m, 2939m, 1637m, 1538m, 1431m, 1186m, 1120s, 1026m, 941m, 858m, 723m, 667w, 547m, 491w, 426w.

2.3. *Synthesis of $[Cu(APTPH_4)(2,2'\text{-bipy})(H_2O)] \cdot 2.63H_2O$ (2)*

A mixture of CuO (0.0199 g, 0.25 mmol), $APTPH_6$ (0.0748 g, 0.25 mmol), 2,2′-bipy (0.0391 g, 0.25 mmol), and H_2O (1 mL), was heated at 80°C in a Teflon-lined stainless steel autoclave for 3 days. Blue crystals were collected (yield: 38.9% based on CuO). Anal. Calcd for **2**: C, 26.8; H, 4.4; N, 7.2; Found: C, 26.9; H, 4.4; N, 7.3; Main IR bands (KBr, cm^{-1}): 3450s, 3018bw, 2752w, 2546w, 2339w, 1652m, 1598s, 1533m, 1446m, 1319w, 1189s, 1116s, 1027s, 923s, 773m, 729w, 671w, 563w, 457w.

2.4. *X-ray data collection*

Crystallographic measurements were obtained on a Bruker SMART CCD area-detector diffractometer, at room temperature (293 K) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and double-pass method ø-ω-scan. All data were corrected for absorption using the program SADABS. The structures were solved by direct methods using SHELXS-97 [13]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using SHELXL-97. The hydrogen atoms of carbon and nitrogen were included in calculated positions and refined with isotropic thermal parameters. The other hydrogen atoms were directly obtained from difference Fourier maps. In addition, because of disorder of the lattice water molecules, the occupancy of one oxygen atom (both O4w) is 0.16 and 0.63 in **1** and **2**, respectively.

3. Results and discussion

3.1. *Structure of $Cu[(APTPH_4)(phen)(H_2O)] \cdot 2.16H_2O$ (1)*

The asymmetric unit of **1** is composed of one Cu(II), one $APTPH_4$ anion, one phen molecule, one coordinated water and 2.16 lattice water molecules. The Cu ion is five coordinate in a distorted square pyramid linked by two oxygen atoms (O1 and O4) from the $APTPH_4$ anion, two nitrogen atoms (N2 and N3) from phen, and one oxygen atom from coordinated water (O1w). A section of the structure about **1** is depicted in figure 1. The O1w lies at the apical site of the square pyramid, at a distance of 2.246(2) Å. The other Cu–O distances are 1.913(2) Å for Cu1–O4, 1.944(2) Å for Cu1–O1, shorter than Cu–O1w. Cu–N distances are 2.000(2) and 2.020(2) Å. In **1**, each $APTPH_6$ is doubly deprotonated transferring a proton to the amino-nitrogen $APTPH_4^{2-}$. Two phosphonate oxygen atoms (O1 and O4) are chelated to the Cu(II), and the third phosphate group is uncoordinated.

Supramolecular structures with extensive hydrogen-bonded network are formed among water molecules, the protonated nitrogen atoms and phosphonate oxygen atoms

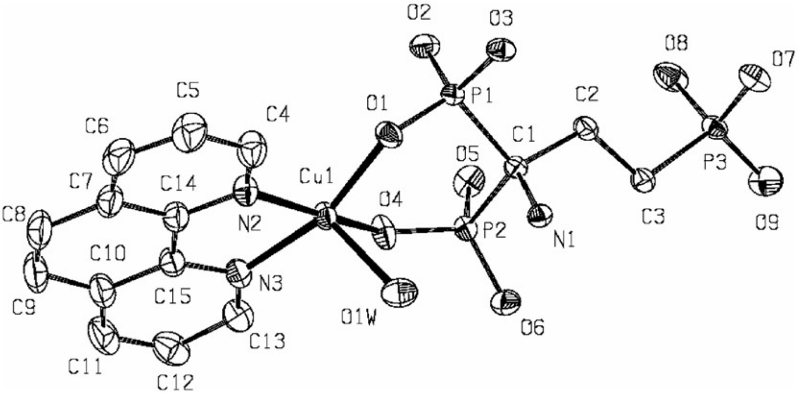

Figure 1. ORTEP view of the coordination geometry of **1** (thermal ellipsoids are at 50% probability). All H atoms are omitted for clarity.

in $APTPH_4^{2-}$ as shown in figure 3. The details of hydrogen bonds are given in table 3. First, dimers are constructed by two relatively strong hydrogen bonds (O2–H8 ⋯ $O7^{\#3}$, 2.455(2) Å and O8–H10 ⋯ $O3^{\#3}$, 2.547(2) Å) between adjacent phosphonate groups of asymmetric units. Then the dimers are connected into a chain along the *b*-axis by hydrogen bonds (O5–H9 ⋯ $O9^{\#4}$, 2.529(2) Å) which are from the phosphonate groups of neighbouring dimers. At the same time, strong hydrogen bonds N1–H3 ⋯ $O3^{\#2}$ (2.723(2) Å), N1–H2 ⋯ $O6^{\#1}$ (2.905(2) Å) and O1W–H1W1 ⋯ $O9^{\#1}$ (2.714(2) Å) between the $APTPH_4$ anions and coordinated water molecules are established to join additional single molecules to chains continuing into the (2D) network. Finally, all water molecules participate in intermolecular hydrogen bonds, which result in forming 3D supramolecular structures. In addition, π–π stacking interactions among the phen rings stabilize the supramolecular structures. The perpendicular distance between adjacent phens is 3.374 Å, and the dihedral angle is zero due to the crystallographic inversion centre. All of these parameters suggest strong π–π interactions.

3.2. *Structure of [Cu(APTPH$_4$)(2,2′-bipy)(H$_2$O)] · 2.63H$_2$O (2)*

The coordination and structure of **2** are similar to **1** except one 2,2′-bipy replaces phen (figure 2). The Cu–O distances range from 1.911(2) to 2.415(2) Å; Cu–N distances are 1.994(2) and 2.001(2) Å. More details of bond distances and angles are given in table 2. The geometry can also be described as a distorted square pyramidal.

Similar to **1**, there is also a diverse hydrogen-bonded network among the water molecules, the protonated nitrogen atoms and phosphonate oxygen atoms in $APTPH_4^{2-}$ (figure 4). The asymmetric units are connected into dimers by strong hydrogen bonds (O3–H8 ⋯ $O9^{\#5}$, 2.491(3) Å) between phosphonate groups of neighboring molecules. Then the dimers are interconnected into an infinite chain along the *b*-axis via hydrogen bonds (O6–H9 ⋯ $O8^{\#4}$, 2.546(3) Å) between phosphonate oxygen atoms. The hydrogen bonds O1W–H1W1 ⋯ $O5^{\#3}$ (2.730(3) Å), N1–H3 ⋯ $O2^{\#2}$ (2.798(3) Å) and O7–H10 ⋯ $O2^{\#2}$ (2.837(4) Å) between coordinated water molecules and phosphonate oxygen atoms, protonated nitrogen atoms from $APTPH_4^{2-}$ connect the chains into a 2D network. Finally, various hydrogen bonds between water molecules and the ligands expand the 2D network into 3D supramolecular structures (table 3). The π–π stacking

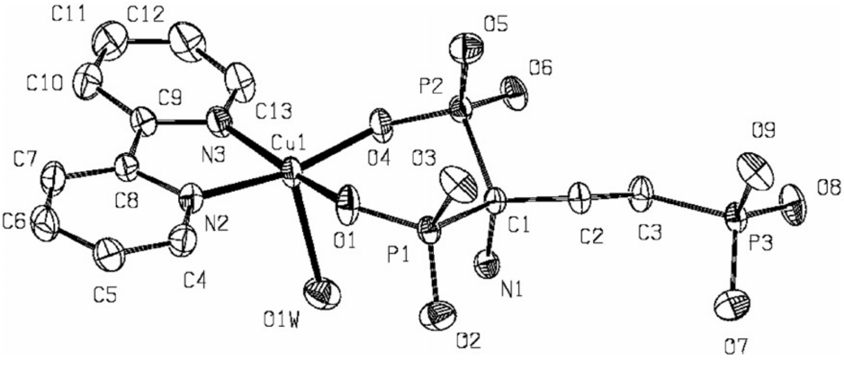

Figure 2. ORTEP view of the coordination geometry of **2** (thermal ellipsoids are at 50% probability). All H atoms are omitted for clarity.

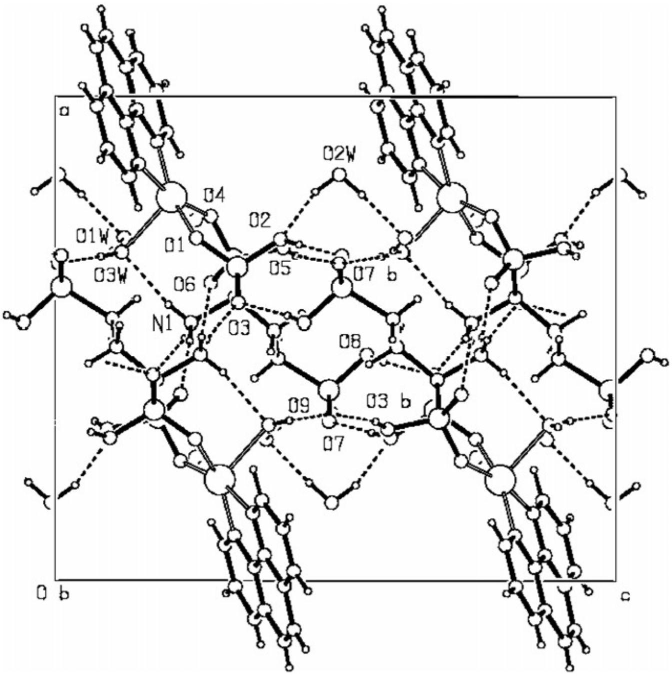

Figure 3. Schematic view of the unit cell of **1** showing the network of hydrogen bonds. Dashed lines represent hydrogen bonds.

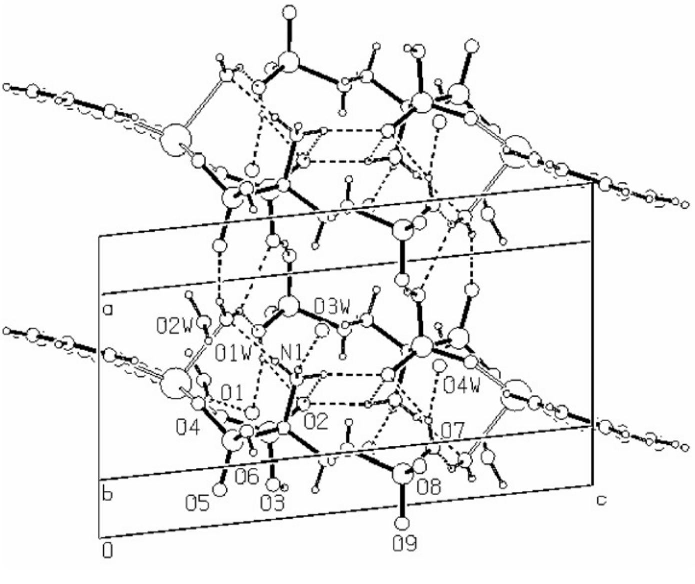

Figure 4. Schematic view of the unit cell of **2** showing the network of hydrogen bonds. Dashed lines represent hydrogen bonds.

interactions along the *a*-axis between 2,2′-bipy rings are also found in **2**, playing an essential role in stabilizing the supramolecular structure. The inter-planar distance (3.283 Å) and dihedral angle (0.02°) between the adjacent 2,2′-bipy suggest π–π interactions are stronger than in **1**.

3.3. *FT-IR spectra*

The IR spectra of these two compounds are similar to each other (see S-2 in supporting information). Both show absorption bands at 3442–3422 cm^{-1}, corresponding to lattice water molecules connected by hydrogen bonds. Broad bands around 2930 cm^{-1} are due to stretching vibrations of the protonated amino. The symmetrical and unsymmetrical vibration bands of PO_2 from PO_3H^- groups in the compounds are observed at about 1151 cm^{-1}. The peaks at 980 cm^{-1} are assigned to υ_s (PO_3) [15]. Bands centered at 2330 and 1050 cm^{-1} are attributed to PO–H and POH vibrations, due to protonated POH groups in the compounds [16, 17]. A series of characteristic peaks in the range of 1425–1630 cm^{-1} are attributed to phen in **1** and 2,2′-bipy in **2** [18].

3.4. *Thermogravimetric study*

The TGA diagram of **1** indicates two main steps of weight losses (figure 5). The first starting at 94°C and ending at 235°C, corresponds to the release of 2.16 lattice water and one coordinated water molecule. The observed weight loss of 9.68% is slightly larger than the calculated value (9.49%). The second step from 235 to 1037°C corresponds to decomposition of $APTPH_4^{2-}$ ligands and phen. The final products are assumed to be $Cu_2P_2O_3$, the observed total weight loss of 48.76% is less than the calculated value of 50.99%. The TGA curve of compound **2** is similar to compound **1**

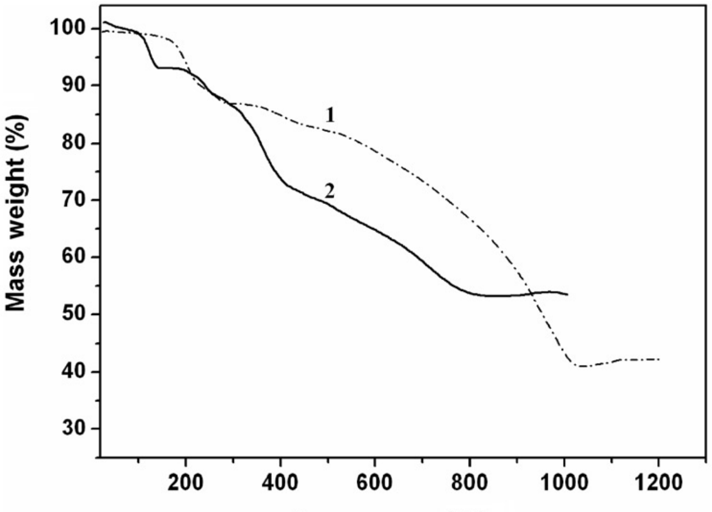

Figure 5. TGA diagrams of **1** and **2**.

Table 1. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{15}H_{24.32}CuN_3O_{12.16}P_3$	$C_{13}H_{25.26}CuN_3O_{12.63}P_3$
Formula weight	599.77	582.16
Temperature (K)	293(2)	293(2)
Crystal system	*Monoclinic*	*Triclinic*
Space group (Å, °)	$P2_1/c$	$P\bar{1}$
a	14.4830(7)	7.1215(7)
b	9.1721(5)	10.460(1)
c	16.7403(8)	14.671(1)
α	90	82.983(2)
β	90.101(1)	83.882(2)
γ	90	80.617(2)
Volume (Å^3)	2223.8(2)	1065.9(2)
Z, D_{calcd} (g cm^{-3})	4, 1.789	2, 1.814
μ (mm^{-1})	1.269	1.321
$F(000)$	1229	597
Crystal size (mm^3)	$0.34 \times 0.25 \times 0.20$	$0.51 \times 0.22 \times 0.10$
θ range for data collection (°)	2.43 to 28.00	2.31 to 27.50
Reflections collected	14504 [R(int) = 0.0171]	6844 [R(int) = 0.0122]
Data completeness	98.8%	96.7%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5306/2/406	4733/3/383
Goodness-of-fit on F^2	1.058	1.047
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0271$	$R_1 = 0.0337$
R indices (all data)	$R_1 = 0.0307$ $wR_2{}^b = 0.0819$	$R_1 = 0.0385$ $wR_2 = 0.0997$
Largest diff. peak and hole (e Å^{-3})	0.774 and −0.345	0.847 and −0.635

$^aR_1 = [\Sigma(|F_0| - |F_c|)/\Sigma|F_o|$; $^bwR_2 = [\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_0|^2)^2]]^{1/2}$, $w = 1/[\sigma^2|F_0|^2 + (Ap)^2 + Bp]$; $p = [|F_0|^2 + 2|F_c|^2]/3$, where $A = 0.0454$, $B = 1.3334$ for compound **1** and $A = 0.0588$, $B = 0.8109$ for compound **2**.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

	1	2
Cu(1)–O(4)	1.913(2)	1.929(2)
Cu(1)–O(1)	1.944(2)	1.911(2)
Cu(1)–N(2)	2.000(2)	1.994(2)
Cu(1)–N(3)	2.020(2)	2.001(2)
Cu(1)–O(1W)	2.246(2)	2.414(2)
O(4)–Cu(1)–O(1)	94.48(6)	93.61(9)
O(4)–Cu(1)–N(2)	166.50(6)	168.41(9)
O(1)–Cu(1)–N(2)	90.93(6)	91.20(9)
O(1)–Cu(1)–N(3)	162.51(6)	166.4(2)
O(4)–Cu(1)–N(3)	89.79(6)	92.26(9)
N(2)–Cu(1)–N(3)	81.52(7)	80.9(2)
O(1)–Cu(1)–O(1W)	85.73(6)	89.4(2)
O(4)–Cu(1)–O(1W)	92.00(6)	89.77(9)
N(2)–Cu(1)–O(1W)	100.74(7)	100.83(9)
N(3)–Cu(1)–O(1W)	111.10(7)	102.9(2)

with two steps of weight loss. The first step from 85–145°C, corresponds to release of 2.63 lattice water molecules. The observed weight loss of 8.18% is close to the calculated value (8.13%). The second weight loss from 190–825°C corresponds to release of the coordinated water, the decomposition of 2,2′-bipy and $APTPH_4^{2-}$.

Table 3. Hydrogen bonds for **1** and **2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
1[a]				
O(2W)–H(1W2)···O(3W)#5	0.91(3)	1.99(3)	2.863(3)	162(3)
O(5)–H(9)···O(9)#4	0.71(3)	1.84(3)	2.529(2)	163(3)
O(8)–H(10)···O(3)#3	0.71(3)	1.85(3)	2.547(2)	172(4)
O(2)–H(8)···O(7)#3	0.76(4)	1.69(4)	2.455(2)	179(5)
N(1)–H(3)···O(3)#2	0.87(3)	1.89(3)	2.723(2)	159(2)
O(1W)–H(1W1)···O(9)#1	0.80(3)	1.92(3)	2.714(2)	169(3)
N(1)–H(2)···O(6)#1	0.83(3)	2.09(3)	2.905(2)	168(2)
O(2W)–H(2W2)···O(2)	0.89(2)	2.11(2)	2.920(3)	150(3)
O(1W)–H(2W1)···O(3W)	0.74(3)	2.13(3)	2.801(3)	150(3)
N(1)–H(1)···O(1W)	0.87(3)	2.10(3)	2.941(2)	164(2)
2[b]				
O(1W)–H(2W1)···O(7)#2	0.83(5)	2.39(5)	3.117(4)	147(4)
O(1W)–H(2W1)···O(3)#3	0.83(5)	2.34(5)	2.930(3)	128(4)
O(1W)–H(1W1)···O(5)#3	0.84(6)	1.93(6)	2.730(3)	157(6)
O(6)–H(9)···O(8)#4	0.73(6)	1.83(6)	2.546(3)	168(7)
O(3)–H(8)···O(9)#5	0.82	1.70	2.491(3)	161.6
O(7)–H(10)···O(4W)	0.86(5)	2.01(5)	2.819(6)	157(4)
O(7)–H(10)···O(2)#2	0.86(5)	2.42(5)	2.837(4)	111(4)
O(2W)–H(1W2)···O(4W)#1	1.08(2)	1.95(3)	2.889(8)	144(3)
N(1)–H(3)···O(2)#2	0.92(4)	1.92(4)	2.798(3)	158(4)
N(1)–H(2)···O(3W)	0.92(4)	1.95(4)	2.787(4)	151(3)
N(1)–H(1)···O(1W)	0.88(4)	2.04(4)	2.924(4)	178(3)

Symmetry transformations used to generate equivalent atoms:
[a]#1 $-x+1$, $y+1/2$, $-z+1/2$; #2 $-x+1$, $y-1/2$, $-z+1/2$; #3 $-x+1$, $-y+2$, $-z+1$; #4 $-x+1$, $-y+1$, $-z+1$; #5 x, $-y+3/2$, $z+1/2$; [b]#1 $-x+1$, $-y+1$, $-z+1$; #2 $-x+1$, $-y$, $-z+1$; #3 $x+1$, y, z; #4 $-x$, $-y+1$, $-z+1$; #5 $-x$, $-y$, $-z+1$.

The observed weight loss of 39.65% is slightly larger than the calculated value (38.83%) if the final product is $Cu_2P_2O_7$.

4. Conclusions

In summary, two new copper(II) triphosphonates have been prepared and characterized structurally. They have similar supramolecular structures constructed by hydrogen bonds and π–π stacking interactions. Current work continues to synthesize metal triphosphonates and study the factors that affect their structures.

Supplementary data

Drawing was produced with PLATON [14]. A summary of crystallographic data for these two compounds is listed in table 1. CCDC 299392(1) and 299675(2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (Internet) C44 1223 336 033; Email: deposit@ccdc.cam.ac.uk].

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