



# Synthesis of homo and hetero metal-phosphonate frameworks from bi-functional aminomethylphosphonic acid

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## ARTICLE INFO

### Article history:

Received 18 December 2007

Received in revised form

12 March 2008

Accepted 24 March 2008

Available online 27 March 2008

### Keywords:

Metal phosphonates

Two-dimensional polymers

Bimetallic polymer

X-ray crystallography

## ABSTRACT

The reaction between aminomethylphosphonic acid (ampa) and the metal salts of Zn, Cd, Hg, Pb, Ag, and Cu afforded seven metal-phosphonate polymers with unique structural features and includes the synthesis of a bimetallic metal-organic framework (Cu/Ag). The characterization of these metal phosphonates is reported by means of infrared spectroscopy,  $^1\text{H-NMR}$ ,  $^{31}\text{P-NMR}$ , X-ray crystallography, energy dispersive X-ray (EDX), and thermogravimetric analysis (TGA). Individual structural features are compared based on the preferred coordination mode of ampa and the geometrical requirements for each metallic center that manipulates the structural motif.

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## 1. Introduction

Metal-organic frameworks [1] have found wide reaching applications [2–7]. In recent years, considerable interest has been developed in the use of complexing molecules containing phosphonate moieties [8]. Metal phosphonates have potential as ion exchangers, in catalysis and as sensors [9]. Phosphonic acid derivatives make ideal candidates as spacers for metal-organic frameworks as can incorporate virtually any organic group, are prepared by facile syntheses [10] and when combined with a metal precursor afford products that vary structurally from discrete molecules to multi-dimensional polymers [11,12]. Of particular interest are bi-functional phosphonic acids, as the presence of a secondary functional group extends the versatility of metal phosphonates to new and more selective applications and can result in more porous materials [13]. To the best of our knowledge, the coordination properties of aminomethylphosphonic acid (ampa) have rarely been studied [14], although diphosphonic acids with amino groups are known to be good chelating agents and have been well researched [15]. Continuing with our research using functionalized phosphonic acids [16], ampa was prepared to examine how metal choice will affect the structural motif of the metal-phosphonate product. The presence of two different functional groups provides numerous chelation modes (Fig. 1) and we were keen to explore whether this bi-functional ligand could be used to prepare mixed metal polymers. Herein we

report the aqueous synthesis and characterization of metal-phosphonate frameworks from reactions of ampa with metallic precursors of Zn, Cd, Hg, Pb, Ag, and Cu.

## 2. Results and discussion

In contrast to traditional hydrothermal methods [12], we wished to examine the outcome of reactions performed under aqueous conditions with gentle heating. The stoichiometric reactions of ampa with  $\text{ZnCl}_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{Ag}(\text{SO}_3\text{CF}_3)$ ,  $\text{AgNO}_3$  and  $\text{Cu}(\text{SO}_3\text{CF}_3)_2/\text{AgNO}_3$  afford a series of polymeric structures **1–5**, and **7–8**, respectively (Scheme 1). These metal-phosphonate polymers have varied structural motifs for example; interlinked 12-membered cyclic cores of a zinc chloride phosphonate polymer, **1**, and distorted cross-linked hexagonal-shaped rings in polymeric cadmium or lead phosphonates (**2** and **4**). Concluding the series; a rare example of a two-dimensional (2D) mercury phosphonate polymer, **3**, where the ampa ligand bridges two mercury centers and two silver polymers with argentophilic interactions, **5** and **7**. More interestingly, a silver/copper bimetallic framework was isolated from the 1:1:1 reaction of ampa with copper triflate and silver nitrate, **8**.

### 2.1. Discussion of **1**

The reaction of zinc chloride with ampa afforded colorless, monoclinic crystals, (space group  $P2_1/c$ ), of complex **1** in 52% yield

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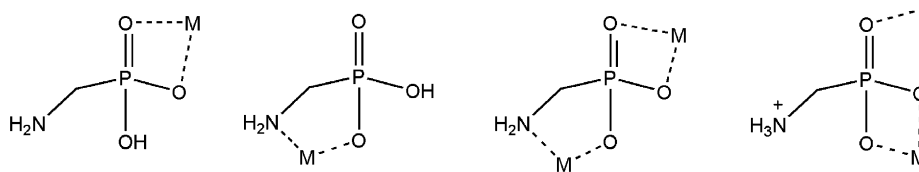
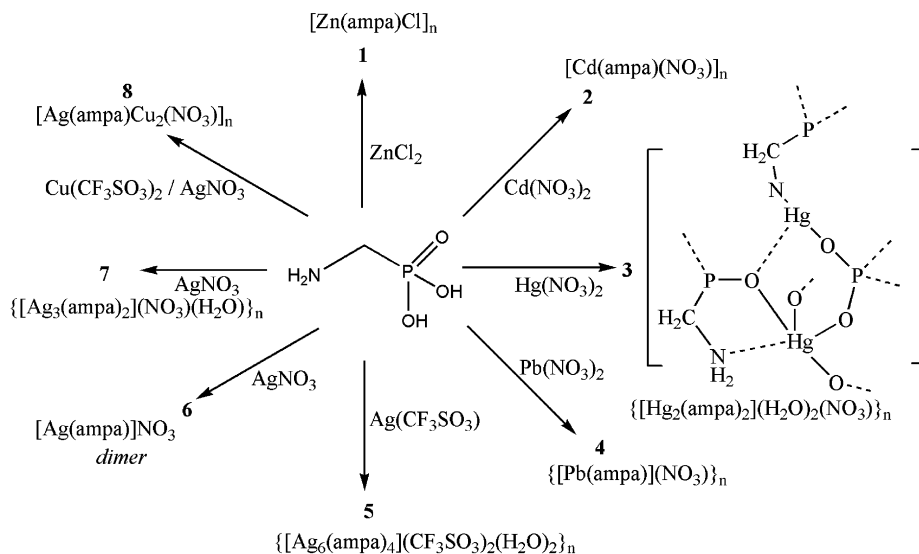


Fig. 1. Possible coordination modes of aminomethylphosphonic acid (ampa).



Scheme 1. Summary of the reactions of ampa with metal precursors.

(Fig. 2). Crystallographic analysis revealed the presence of a zinc bi-dimensional framework with each zinc atom in a distorted tetrahedral environment formed by three oxygen atoms from different ampa molecules and one chlorine atom. The phosphonate group of ampa is doubly deprotonated, but protonated at the amine nitrogen, therefore existing in its zwitterionic form. The existence of the zwitterionic form of the ligand is not too surprising given that a large volume of research has been devoted to employing amines as templating agents for zinc phosphates and phosphonates in which the amines are used for deprotonation of the phosphonic acid and stabilization of the framework through hydrogen bonding [17]. The Zn–O distances are in the range 1.932(2)–1.965(2) Å with each oxygen atom on the phosphonate group coordinated to three different zinc atoms. This affords tetrahedral units of  $[\text{ZnClO}_3]$  and  $[\text{PCO}_3]$  that share common corners creating 12-membered  $[\text{Zn–O–P–O}]_3$  units that is a common feature of zinc phosphonate polymers [18]. The structural motif of **1** is reminiscent of the zinc chlorophosphonate  $[\text{C}_6\text{NH}_{14}][\text{ZnClHPO}_4]$  prepared by hydrothermal methods that like in complex **1**, has chlorine atoms perpendicular to the Zn–O–P units [19].

Around every 12-membered unit, a regular symmetrical arrangement can be seen in which the flanking amino groups are arranged on one side of the cyclic core, while on the flip side terminal halides are observed (Fig. 2). The amine–amine and chloride–chloride separation is 4.755 Å. The structure shows hydrogen bonding between the chlorine atom and the amino nitrogen atom, as well as between one of the amine hydrogen atoms and O(2) of the phosphonate group (Table 1).

The absence of solvent molecules in **1** affords a thermally stable polymer that has no solvent accessible voids and decomposes at 220–221 °C. The thermal stability is confirmed by thermogravimetric analysis (TGA) analysis where minimal

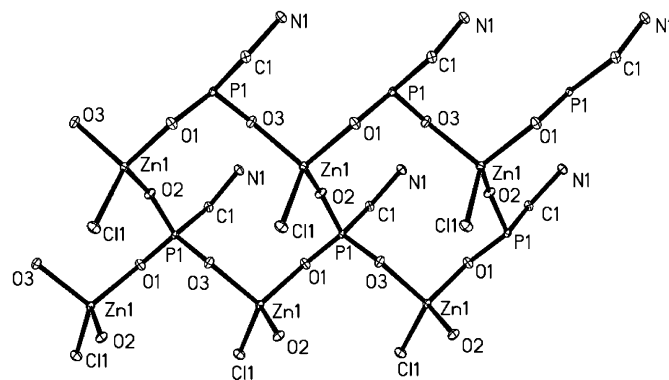


Fig. 2. Thermal ellipsoid plot of the structural motif of **1**. Hydrogen atoms are omitted for clarity, thermal ellipsoids at 30% probability. Selected bond lengths (Å) and angles (°): Zn(1)–O(1) 1.944(2), Zn(1)–O(2) 1.932(2), Zn(1)–O(3) 1.965(2), Zn(1)–Cl(1) 2.2479(8), P(1)–O(1) 1.516(2), P(1)–O(3a) 1.517(2), P(1)–O(2a) 1.523(2), O(1)–Zn(1)–O(2) 116.26(8), O(2)–Zn(1)–O(3) 98.31(8), O(1)–Zn(1)–O(3) 105.52(8), O(1)–Zn(1)–Cl(1) 113.74(6), O(3)–Zn(1)–Cl(1) 116.80(6), O(1)–P(1)–O(3) 114.23(11), O(1)–P(1)–C(1) 104.70(12).

Table 1  
H-bonding interactions in **1**

Donor (D) H-acceptor (A)	H..A (Å)	D..A (Å)	D..H (Å)
N1–H1C..O2	1.98(4)	2.916(3)	166(3)
N1–H1D..Cl1	2.43(5)	3.258(3)	154(4)
N1–H1G..Cl1	2.72(4)	3.336(3)	130(3)
N1–H1G..O1	2.52(3)	3.037(3)	119(3)

weight loss (0.49%) is observed from 50 to 200 °C, followed by a sharp weight loss, corresponding to decomposition of the ligand.

## 2.2. Discussion of 2

Under similar conditions to the synthesis of **1**, polymer **2** (Fig. 3) was isolated from the 1:1 reaction of ampa and cadmium(II) nitrate. The cadmium halide precursor was exchanged for the nitrate salt because following the structural analysis of **1** it was thought that the terminal halide was limiting polymer dimensionality, thus employing the coordinating nitrate anion may lend itself to higher dimensional structures.

The isolated 2D cadmium phosphonate polymer displays the cadmium atom in a distorted octahedral coordination sphere consisting of cadmium atoms bonded to an oxygen atom from a nitrate ion and two oxygen atoms from the phosphonate group of the ampa ligand. The symmetry-related equivalents of these oxygen atoms make up the slightly distorted octahedral arrangement. This slight distortion is attributed to the steric constraints that are imposed by the small bite angle of the ampa group and its limited flexibility. The change from tetrahedral geometry observed around  $Zn^{2+}$  in **1** to octahedral geometry around  $Cd^{2+}$  in **2** is likely to be associated with the size effect comparing the ionic radii of  $Zn^{2+}$  (0.74 Å) and  $Cd^{2+}$  (0.97 Å) [20].

The cadmium polymer, **2**, displays three different Cd–O bond lengths, all within expected ranges [21], and also includes a Cd–P interaction at a distance of 2.9999(12) Å, which is within the sum of their van der Waals radii (3.38 Å) [21e]. The oxygen atom, O(4), and the amino nitrogen atom have disorder associated with a mirror plane, which causes a symmetry equivalent to the one on growing the polymer, but were satisfactorily refined at half occupancy. The longest Cd–O bond at 2.420(2) Å corresponds to the shortest P–O bond (1.514(3) Å). For charge balance the ligand is doubly deprotonated which is reflected by the P–O bond lengths of P(1)–O(1) and P(1)–O(1a) at 1.528(2) Å, this results in the zwitterionic form of the ligand, with protonation at the nitrogen atom, N(1). The hydrogen atoms on the nitrogen atom were located from the residual electron density difference map, using the non centro-symmetric space group,  $Pna2_1$  [22].

The unique environment for the phosphorus atoms is confirmed by the presence of a single peak at 12.30 ppm in the  $^{31}P$ -NMR solution experiment, which can be compared to that of the free ligand, which has a  $^{31}P$  chemical shift at 11.49 ppm. The presence of only one peak in the  $^{31}P$ -NMR suggests that the polymer remains intact in solution. In cases where ligand loss occurs coinciding with polymer decomposition, usually several peaks are observed in the spectrum. Solid-state infrared spectroscopy revealed strong absorptions in the 1000–1200  $cm^{-1}$  corresponding to P=O and P–O stretching vibrations [23]. The

cadmium phosphonate polymer is thermally robust, not melting at 250 °C. TGA analysis confirms this, with negligible weight loss from 50 to 300 °C.

## 2.3. Discussion of 3

Mercury(II) as a typically soft cation prefers coordination to soft nitrogen atoms [28]. Given the bi-functional nature of ampa we wished to explore the reaction of ampa with  $Hg(NO_3)_2$ ; firstly, to determine the coordination preference of Hg(II) for comparison with Cd and Zn, but also because reports on mercury(II) phosphonates are disproportionately sparse when compared with that of other metals [24]. This is likely to be due to the low solubility of mercury salts and the difficulty in isolating suitable single crystals for X-ray diffraction [26].

From the equimolar reaction of  $Hg(NO_3)_2$  with ampa, colorless crystals of a 2D mercury polymer were isolated in 21% yield (Fig. 4). The mercury polymer, **3**, differs from the previous zinc and cadmium polymers, because in **3**, one ampa molecule is found to bridge two mercury centers with one mercury atom coordinated to the amine group, while a second mercury center is coordinated to the phosphonate oxygen atoms (Fig. 4).

An interesting feature of this polymer is that the mercury atoms are in two very distinctive environments. In one case, the mercury atom, Hg(1), is five coordinate, with the sites occupied by a nitrogen atom from an amine group and  $\mu_2$  oxygen atoms from the ampa. This type of geometry is a common occurrence for mercury complexes [22]. The second environment found for mercury is less well observed [23] and Hg(2) has seesaw geometry, with the N(2)–Hg(2)–O(6) angle, close to linear (176.6(3)°). The coordination sphere around Hg(2) consists of a nitrogen atom and two bridging oxygen atoms from the phosphonate group. The uncoordinated oxygen O(2) atom on P(1) remains protonated, as evidenced by the longer P–O bond of 1.538(8) Å. The net charge of the framework is balanced by the presence of guest nitrate ions in the lattice.

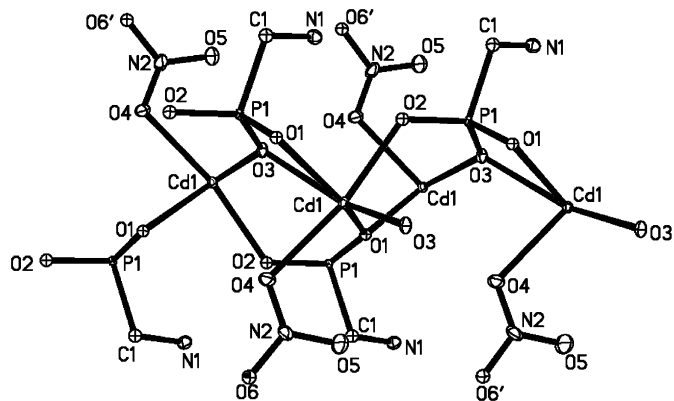
The Hg–O bonds vary from 2.117(7) to 2.656(7) Å with those at the longer end substantiating the presence of a weak interaction, the Hg–N bonds av. 2.123 Å correspond well to documented Hg–NH<sub>2</sub> interactions [27]. A distance of 3.860 Å separates the mercury atoms, which is longer than the sum of their van der Waals radii (rrdW = 1.73 Å) [24].

Interestingly, despite the different mercury environments, the phosphorus atoms exist in almost identical environments with similar bond lengths and angles. The mercury phosphonate, **3**, has moderate solid-state thermal stability melting at 150–152 °C. TGA confirmed this with sharp weight loss (56.4%) between 176 and 180 °C corresponding with decomposition of the polymer. In solution the mercury phosphonate has lower stability, with mercury deposition observed at ~80–85 °C.

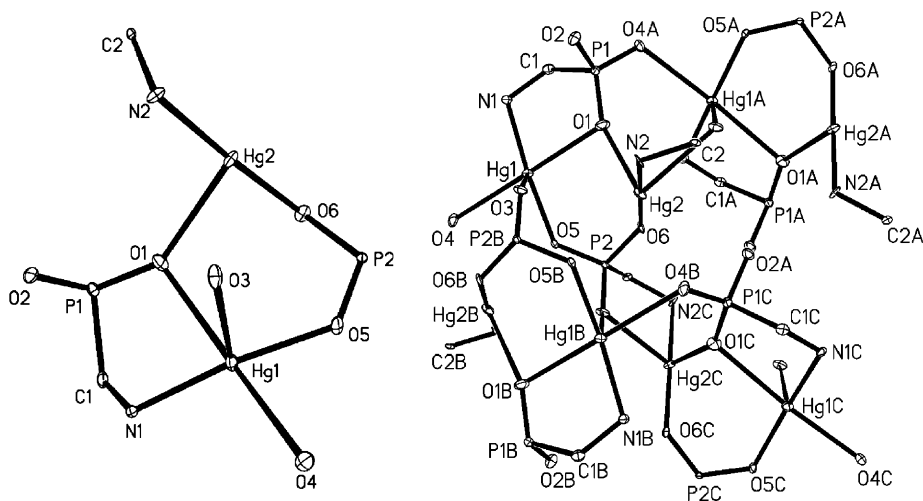
Following our initial success with the heavier transition metal atoms, we decided to explore the use of lead nitrate as a possible metallic precursor for comparison with the common oxidation state (2+) of Zn, Cd, and Hg. Furthermore, studies have shown that Pb(II) exhibits different structural chemistry from those of the 2+ transition metals due to the presence of the lone pair of electrons [25,29]. This was tested by the aqueous, stoichiometric reaction of  $Pb(NO_3)_2$  and ampa.

## 2.4. Discussion of 4

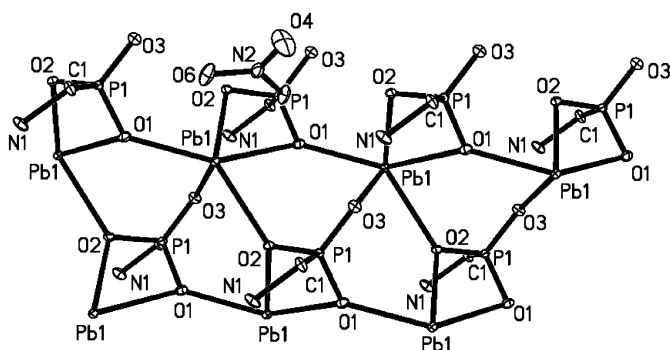
The 1:1 aqueous reaction of  $Pb(NO_3)_2$  and ampa afforded, **4**, a 2D lead phosphonate polymer (Fig. 5). It is noteworthy to mention that although lead phosphonates have been previously reported



**Fig. 3.** Polymeric form of **2**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cd(1)–O(1)#1 2.198(2), Cd(1)–O(2) 2.312(3), Cd(1)–O(3) 2.374(4), P(1)–O(1) 1.528(2), O(2)–Cd(1)–O(3) 169.78(12), O(2)–Cd(1)–O(1) 88.01(9).



**Fig. 4.** Solid-state diagram of **3** depicting the atom connectivity. Selected bond lengths (Å) and angles (°): Hg(1)–O(1) 2.589(8), Hg(1)–O(3) 2.473(8), Hg(1)–O(4) 2.526(7), Hg(1)–O(5) 2.117(7), Hg(1)–N(1) 2.144(8), Hg(2)–O(1) 2.542(7), Hg(2)–O(6) 2.059(7), Hg(2)–N(2) 2.103(8), P(1)–O(1) 1.513(8), P(1)–O(2) 1.538(8), P(2)–O(5) 1.528(7), P(2)–O(6) 1.537(7), O(5)–Hg(1)–N(1) 164.9(3), N(1)–Hg(1)–O(1) 77.3(3), O(4)–Hg(1)–O(1) 170.9(2), O(6)–Hg(2)–N(2) 176.4(3), O(6)–Hg(2)–O(1) 80.7(3).



**Fig. 5.** Polymeric arrangement of **4** (thermal ellipsoids at 30% probability level). H atoms and nitrate counter ions are omitted for clarity. Pb(1)–O(1) 2.716(6), Pb(1)–O(2) 2.411(6), P(1)–O(1) 1.525(6), P(1)–O(2) 1.539(6), P(1)–O(3) 1.521(6), O(1)–Pb(1)–O(1a) 137.68(17), O(1)–Pb(1)–O(2) 83.2(2), O(3)–P(1)–O(2) 115.0(4).

the majority of these are prepared using harsh hydrothermal methods [30], in contrast to the aqueous synthesis of **4**.

Each lead atom is five coordinate in distorted square pyramidal geometry with oxygen atoms at each vertex and the open side of the pyramid occupied by a lone pair of electrons. The electrostatic repulsions of the lone pair leads to the distorted geometry. The Pb–O distances are in the range 2.356(6)–2.716(6) Å and are comparable with related systems, the Pb–Pb separation is 4.612 Å which is too long for any metal–metal interaction [31]. In a similar fashion to the zinc and cadmium polymers, the ampa ligand exists in its zwitterionic form with the phosphonic acid oxygen atoms doubly deprotonated and a protonated NH<sub>2</sub> group. The charge is balanced by the presence of lattice nitrate ions. A further similarity between the cadmium and lead polymers is the metal–phosphonate repeating unit, which consists of distorted hexagonal-shaped rings, as depicted in Fig. 6, which also emphasizes the distorted geometry around the lead atoms.

## 2.5. Discussion of **5**

Continuing with the exploration of the late transition metals, polymer **5** was obtained from the reaction between silver triflate and ampa in a 1:1 molar ratio. Silver amino phosphonate polymers appear less well characterized than other transition

metals, in fact, a survey of the CCDC revealed only one, from the reaction of silver nitrate with *N*-phosphonomethyl glycine [32].

Complex **5** crystallizes as colorless needles in the triclinic space group, *P* $\bar{1}$  (Fig. 7). Solid-state analysis of **5** shows six silver atoms in the asymmetric unit, each adopting five coordinate geometry. Four ampa molecules support these six silver atoms, and two triflate anions in the lattice balance the cationic metal charge.

The three oxygen atoms on each of the four ampa molecules all coordinate to different silver atoms; for example, the three oxygen atoms on P(1) coordinate to Ag(6), Ag(2), and Ag(1) through O(1), O(2), and O(3), respectively. The phosphorus–oxygen bond lengths are varied, ranging from 1.504(6) to 1.537(5) Å. It is possible that some of the P–O bonds remain protonated, however, no hydrogen atoms for these oxygen atoms could be located.

The repeating unit of polymer **5**, consists of a ‘silver column’ that is generated through edge-sharing triangles (Fig. 8). Similar arrangements of Ag atoms have been observed but most of these are in cages and clusters rather than a polymeric system [33]. The Ag–Ag bonds are in the range 2.9181–3.1642 Å that are suggestive of argentophilic interactions [34]. The existence of these argentophilic interactions prompted us to investigate the luminescence of this system as luminescence of Ag–Ag compounds is a well-known phenomenon, that in part is attributed to the existence of argentophilic interactions [35]. The solution state luminescence was probed at various excitation wavelengths; however, no luminescence was observed, but it is possible that low-temperature measurements are required.

The presence of non-coordinating guest ions reduce the thermal robustness of the system with complex **5** melting at 140–142 °C. However, their presence does promote extensive hydrogen bonding which can be observed between the NH<sub>2</sub>-triflate groups, and the phosphonate oxygen atoms with adjacent NH<sub>2</sub> groups. The decreased thermal robustness of **5** is evidenced from TGA data that showed 1.28% weight loss from 117 to 180 °C, which is close to the loss of H<sub>2</sub>O, theoretical value = 1.25%. Broad IR adsorption bands are observed at 3451 cm<sup>-1</sup> confirming the presence of lattice water molecules.

## 2.6. Discussion of **6** and **7**

Following the isolation of polymer **5** that has lattice triflate ions, we wished to investigate whether more porous and robust

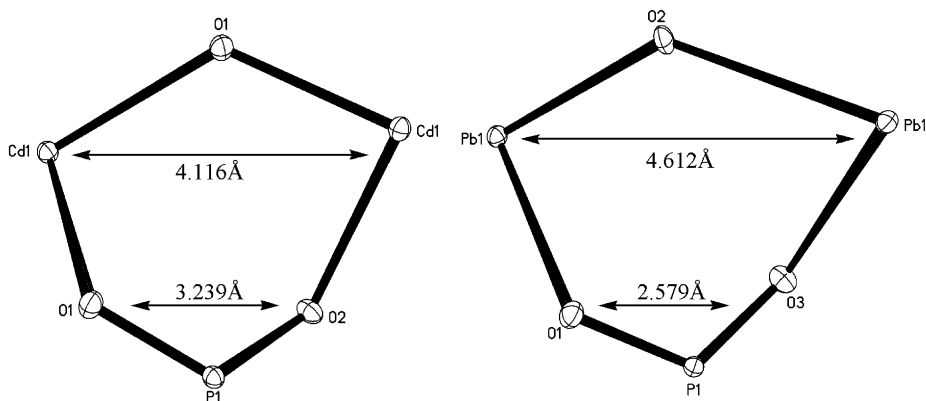


Fig. 6. Hexagonal-shaped rings in the cadmium and lead polymers, 2 and 4.

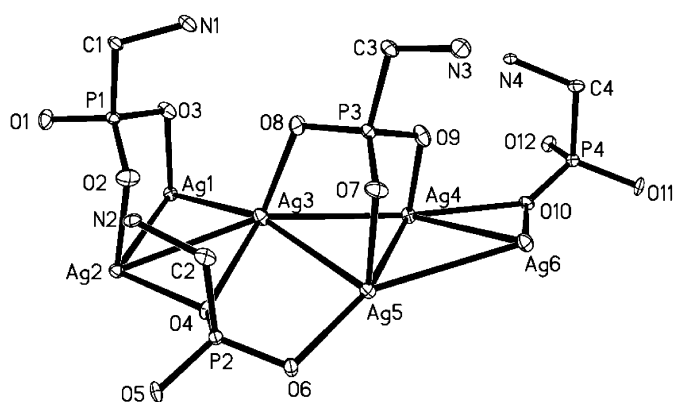


Fig. 7. Structural motif of 5 (thermal ellipsoids shown at 30% probability, triflate anions, H atoms and lattice water molecules are omitted for clarity.) P(1)–O(1) 1.504(6), P(1)–O(2) 1.526(6), P(1)–O(3) 1.518(5), Ag(1)–O(3) 2.225(5), Ag(2)–O(2) 2.184(6), Ag(2)–O(4) 2.515(5), O(3)–Ag(1)–O(5)#3 85.63(19), O(8)–Ag(3)–O(5) 104.81(18), O(6)–Ag(4)–O(9) 105.76(19).

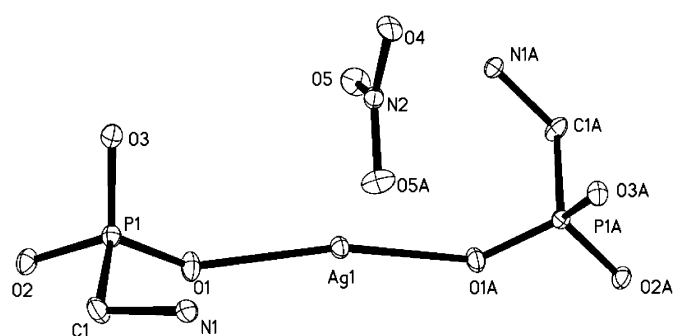


Fig. 9. Coordination environment of silver in 6. Hydrogen atoms are omitted for clarity. Thermal ellipsoids drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Ag(1)–O(1) 2.320(3), P(1)–O(1) 1.498(3), P(1)–O(2) 1.569(3), P(1)–O(3) 1.505(3), O(1)–Ag(1)–O(1A) 162.60(14), O(3)–P(1)–O(1) 116.01(17).

were only able to obtain a mixture of the same two products. To determine which is the major product the reaction was repeated several times and the crystals were separated by hand using the microscope. In all cases, polymeric 7 was found to be the major product, ~78–83%.

The major product of the reaction, complex 7 crystallizes in monoclinic space group  $C2/c$  and the single-crystal analysis revealed a polymeric species displaying a triangular arrangement of silver atoms, each in distorted octahedral environments with argentophilic interactions (Figs. 10 and 11).

The asymmetric unit in 7 has three crystallographically unique silver atoms coordinated to two ampa ligands with a lattice nitrate ion and one molecule of water. Each silver atom is found to adopt seven coordinate geometry with sites occupied by four oxygen atoms and three different silver atoms with Ag–Ag distances in the range 2.997–3.268 Å (Fig. 11). The triangular arrangement of silver atoms observed in 7 is not uncommon for silver coordination polymers with many examples reported with similar Ag–Ag bond lengths to those recorded in 7 [37].

After considering the various possible coordinate modes of ampa including the N–Hg coordination observed for mercury, we wished to explore the viability of this bi-functional phosphonic acid for bimetallic phosphonate syntheses. We anticipated that through careful selection of the metal precursor, ampa could be used to coordinate different metal centers through both the  $NH_2$  and phosphonate group. To this end, ampa was reacted with silver nitrate and copper(II) triflate in a 1:1:1 ratio and afforded crystalline material of a bimetallic framework, 8. Polymer 8 joins a fairly limited number of structurally characterized bimetallic polymers (Figs. 12 and 13) [38].

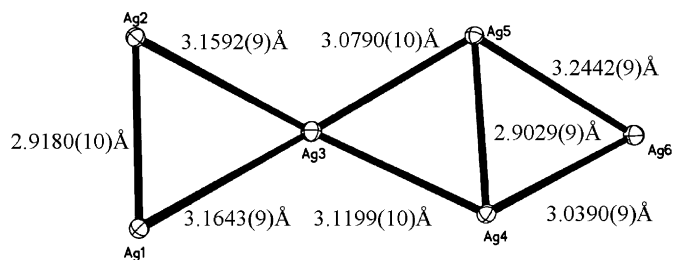
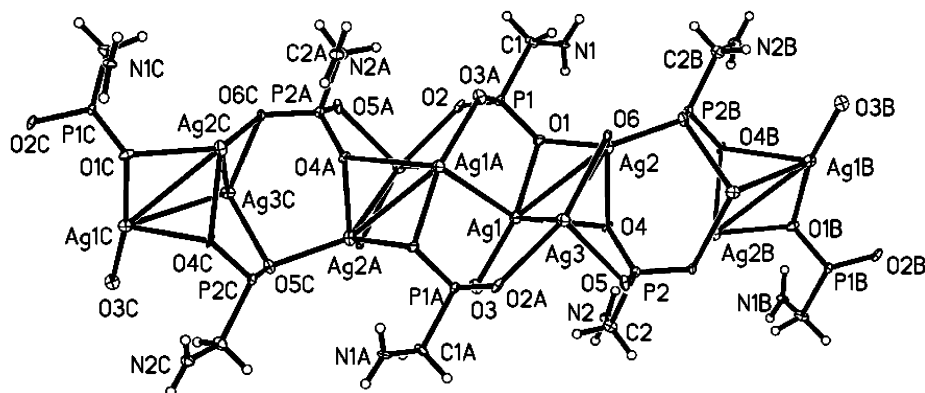


Fig. 8. Arrangement of silver atoms in 5.

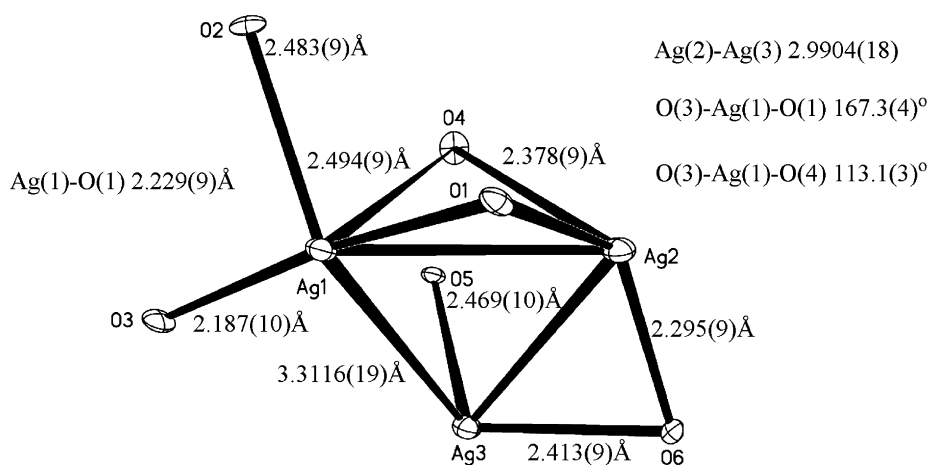
materials could be obtained through exchange of the metal precursor. This is because the presence of solvent molecules and anions in the crystalline lattice limit porosity [36], therefore, in order to harness any future potential applications we wished to investigate the reactions of ampa with a series of silver precursors.

The reaction of silver nitrate with ampa (1:1) afforded two different products, a monomeric Ag–ampa complex, 6 (Fig. 9) and a silver phosphonate polymer, 7 (Fig. 10). These two compounds were obtained from the same reaction vial and were identified under the microscope as two different crystal types. Attempts to separate them by recrystallization were unsuccessful, as were attempts to optimize the yield of each product through reaction temperature. The reaction was performed at room temperature, low temperature (0 °C), and high temperature (100 °C) but we





**Fig. 10.** Polymeric structure of **7**, thermal ellipsoids at 30% probability level. Bond lengths (Å) of the phosphonate groups: P(1)–O(1) 1.531(10), P(1)–O(2) 1.525(9), P(2)–O(4) 1.527(10), P(2)–O(5) 1.529(9).



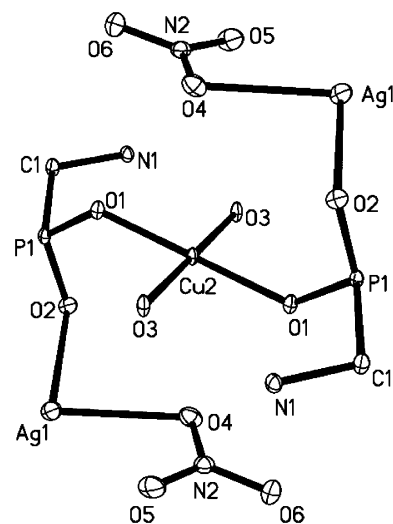
**Fig. 11.** Diagram to depict coordination environment, bond lengths (Å) and angles (°) of the silver atoms in **7**. Thermal ellipsoids are drawn at 30% probability level.

Examination of the crystal structure showed that the silver atoms exhibit square pyramidal geometry while the copper atoms are found in square planar geometry. The oxygen atoms coordinated to the silver atom arise from nitrate anions coordinating in a  $\mu_2$  and  $\mu_1$  fashion. The phosphonate oxygen atoms, O(1) and O(2), bridge the Ag and Cu atoms. The Ag–O and Cu–O distances are as expected and are in the range 2.353–2.585 and 1.938(2)–1.950(2) Å, respectively [39]. The overall 3+ charge from the metal atoms, is balanced by a doubly deprotonated phosphonate group and a nitrate anion. Hydrogen bonding can be observed between the amine group, N(1)–H(1), and O(3) of the phosphonate moiety (dH...A, 2.01 Å, dD...A, 2.863(3) Å).

To further confirm the presence of the same bimetallic framework in the crude product, energy dispersive X-ray (EDX) analysis was performed and confirmed the presence of both copper and silver; however, sulfur contamination from the triflate precursor was also observed (EDX spectrum is shown in Supplementary material).

### 3. Conclusions

As a result of exploring the chemical behavior of ampa in reactions with different metal salts, it was possible to isolate seven novel metal-phosphonate polymers. These polymers display specific geometrical characteristics according to the stereochemical requirements of the metallic center, the organic ligand and in some cases, the presence of counterions. The diverse



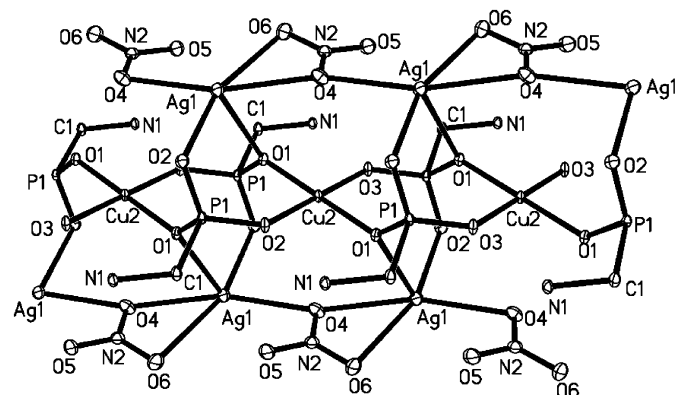
**Fig. 12.** Coordination environments of silver and copper in **8**. Selected bond lengths (Å) and angles (°). Cu(2)–O(1) 1.939(2), Cu(2)–O(3) 1.950(2), P(1)–O(1) 1.537(2), P(1)–O(2) 1.514(2), Ag(1)–O(2) 2.353(2), Ag(1)–O(4) 2.513(3), O(1)–Cu(2)–O(1) 180.0, O(1)–Cu(2)–O(3) 89.50(9), O(2)–Ag(1)–O(4) 85.73(8).

structural motifs observed in **1–8** emphasize the varying coordination abilities of the versatile ampa ligand. These coordination modes include: its zwitterionic form with zinc, cadmium and

lead, acting as a bridging ligand between two mercury atoms, linking two different metal centers, Cu/Ag, and remaining singly or doubly protonated and coordinating through one or two phosphonate oxygen atoms with silver. Future work will involve the further study of bimetallic phosphonate polymers and whether extending the length of the carbon chain to aminoethyl-phosphonic acid or aminopropyl phosphonic acid will lead to more porous structures.

### 3.1. Experimental

**Materials and methods:** ampa was prepared using modified literature methods [10]. Other materials were purchased from Aldrich and used as received. IR spectra were recorded from KBr pellets on a FT-IR spectrometer. TGA were carried out on a Seiko 220 instrument at a heating rate of 5 °C/min.  $^1\text{H}$ ,  $^{31}\text{P}\{\text{H}\}$  were recorded in solution on a Varian 300 MHz. No meaningful  $^{13}\text{C}$  data could be collected. Fluorescence was recorded using a Shimadzu 5301PC spectrofluorimeter at ambient temperature. Elemental Analysis was performed by Schwarzkopf Microanalytical Lab, NY and was determined for all complexes excluding **6** and **7**.



**Fig. 13.** Polymeric arrangement of the bimetallic phosphonate, **8**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids drawn at 30% probability level.

### 3.2. X-ray crystallography

Data collection of the compounds were performed at  $-60\text{ }^\circ\text{C}$  on a Bruker SMART 1000, Mo  $K\alpha$  (0.71073 Å) equipped with cryostream. *SAINTE* was used for data reduction and cell refinement [40], *SADABS* [40] was run for absorption correction on all data. Crystal structures were solved using direct methods and refined with full-matrix least-squares treatment (SHELXL) [40]. Crystal data for **1–8** is provided in Tables 2–4.

### 3.3. Synthesis of **1**, $[\text{Zn}(\text{ampa})\text{Cl}]_n$

Ampa (0.1 g, 0.9 mmol) and  $\text{ZnCl}_2$  (0.12 g, 0.9 mmol) were added together in an open vial containing 3 mL of water. The reaction mixture was stirred and heated at  $70\text{ }^\circ\text{C}$  for 1 h. After 1 h, the reaction mixture was filtered to remove any insoluble material. The final pH of the solution was 3. Colorless crystals suitable for X-ray crystallography analysis were obtained by slow evaporation from the colorless solution at ambient temperature. Yield: 0.092 g, 52% based on  $\text{ZnCl}_2$ . M.P.  $220\text{--}221\text{ }^\circ\text{C}$  (decomposition). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3565 (s), 3478 (s), 3215 (s), 3143 (s), 2957 (m), 2930 (m), 2900 (w), 1625 (m), 1480 (s), 1421 (s), 1382 (m), 1252 (s), 1192 (s), 1105 (s), 1051 (s), 835 (m), 797 (m), 741 (s), 700 (m).  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ , 300 MHz,  $25\text{ }^\circ\text{C}$ ) 3.05 ppm (d, 2H,  $J = 12.6\text{ Hz}$ ).  $^{31}\text{P-NMR}$  12.16 ppm (s).

### 3.4. Synthesis of **2**, $[\text{Cd}(\text{ampa})(\text{NO}_3)]_n$

Ampa (0.05 g, 0.5 mmol) and  $\text{Cd}(\text{NO}_3)_2$  (0.14 g, 0.5 mmol) were added together in an open vial containing 3 mL of water. The reaction mixture was stirred and heated at  $100\text{ }^\circ\text{C}$  for 1 h. After 1 h, the reaction mixture was filtered and the pH recorded (pH = 3). Suitable crystals for X-ray crystallography were obtained from the solution. Yield = 0.036 g, 27% based on  $\text{Cd}(\text{NO}_3)_2$ . The product has a melting point above  $250\text{ }^\circ\text{C}$ . IR (KBr pellet,  $\text{cm}^{-1}$ ): 3561 (m), 3478 (m), 3238 (s), 3094 (m), 2805 (m), 2698 (m), 2611 (m), 2565 (m), 2344 (w), 2128 (w), 1622 (m), 1606 (s), 1523 (s), 1363 (s), 1252 (m), 1191 (s), 1101 (s), 865 (w), 827 (m), 816 (m), 739 (s).

**Table 2**  
Crystal data for compounds **1–3**

Compound name	<b>1</b>	<b>2</b>	<b>3</b>
Chemical formula	$\text{C}_7\text{H}_4\text{ClNO}_3\text{PZn}$	$\text{C}_7\text{H}_4\text{CdN}_3\text{O}_7\text{P}$ [22]	$\text{C}_8\text{H}_{36}\text{N}_{10}\text{O}_{36}\text{P}_8\text{Hg}_8^{\text{a}}$
Formula weight	210.85	279.40	2700.95
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pnma$	$C2/c$
$T$ (K)	213(2)	213(2)	213(2)
$a$ (Å)	4.7551(6)	19.995(3)	23.418(3)
$b$ (Å)	15.6652(19)	6.2770(10)	10.5542(12)
$c$ (Å)	8.1084(9)	5.1508(8)	10.1938(12)
$\alpha$ (°)	90	90	90
$\beta$ (°)	107.225(6)	90	108.855(2)
$\gamma$ (°)	90	90	90
$V$ (Å <sup>3</sup> )	576.90(12)	646.46(18)	2384.2(5)
$Z$	4	4	2
Reflections collected	3228	3609	6549
Independent reflections	1309	830	2779
Data/restraints/parameter ratio	1309/0/85	830/0/71	2779/9/169
Unique data ( $R_{\text{int}}$ )	0.0319	0.0345	0.0433
$D_{\text{calc}}$ ( $\text{mg}/\text{m}^3$ )	2.428	2.871	3.762
$F(000)$	416	524	2404
$R$ indices (all data)	$R_1 = 0.0310$ , $wR_2 = 0.0650$	$R_1 = 0.0272$ , $wR_2 = 0.0692$	$R_1 = 0.0558$ , $wR_2 = 0.1038$
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0269$ , $wR_2 = 0.0631$	$R_1 = 0.0263$ , $wR_2 = 0.0685$	$R_1 = 0.0391$ , $wR_2 = 0.0940$
Largest difference in peak and hole ( $\text{e}/\text{Å}^3$ )	0.605 and $-0.704$	1.163 and $-1.054$	3.142 and $-3.630^{\text{b}}$

<sup>a</sup> H atoms that were not included in the refinement are not included in the chemical formulas.

<sup>b</sup> The large electron density peaks remaining are in close proximity to the heavy metal atom.

**Table 3**  
Crystal Data for compounds 4–6

Compound name	4	5	6
Chemical formula	C <sub>1</sub> H <sub>5</sub> N <sub>2</sub> O <sub>6</sub> P <sub>1</sub> Pb	C <sub>6</sub> H <sub>16</sub> Ag <sub>6</sub> F <sub>6</sub> N <sub>4</sub> O <sub>21</sub> P <sub>4</sub> S <sub>2</sub>	C <sub>2</sub> H <sub>10</sub> AgN <sub>3</sub> O <sub>9</sub> P <sub>2</sub>
Formula weight	379.23	1429.45	389.94
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>Pbcn</i>
<i>T</i> (K)	213(2)	213(2)	213(2)
<i>a</i> (Å)	5.1448(10)	7.2789(12)	5.6075(4)
<i>b</i> (Å)	19.182(4)	10.8120(18)	9.0707(7)
<i>c</i> (Å)	8.7258(13)	20.404(3)	21.4778(15)
$\alpha$ (°)	90	89.088(3)	90
$\beta$ (°)	124.668(8)	83.609(3)	90
$\gamma$ (°)	90	88.886(3)	90
<i>V</i> (Å <sup>3</sup> )	708.2(2)	1595.3(5)	1092.45(14)
<i>Z</i>	4	2	4
Reflections collected	3948	9809	5849
Independent reflections	1662	7095	1325
Data/restraints/parameter ratio	1662/1/112	7095/0/437	1325/1/83
Unique data ( <i>R</i> <sub>int</sub> )	0.0412	0.0292	0.0312
<i>D</i> <sub>calc</sub> (mg/m <sup>3</sup> )	3.557	2.976	2.182
<i>F</i> (000)	680	1352	768
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0456, <i>wR</i> <sub>2</sub> = 0.0803	<i>R</i> <sub>1</sub> = 0.0867, <i>wR</i> <sub>2</sub> = 0.1238	<i>R</i> <sub>1</sub> = 0.0427, <i>wR</i> <sub>2</sub> = 0.0915
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0345, <i>wR</i> <sub>2</sub> = 0.0760	<i>R</i> <sub>1</sub> = 0.0492, <i>wR</i> <sub>2</sub> = 0.1062	<i>R</i> <sub>1</sub> = 0.0340, <i>wR</i> <sub>2</sub> = 0.0870
Largest difference in peak and hole (e/Å <sup>3</sup> )	2.576 and −1.918 <sup>a</sup>	1.588 and −1.290	1.102 and −0.657

<sup>a</sup> The large electron density peaks remaining in the difference map is associated with the heavy metal center.

**Table 4**  
Crystal data for 7 and 8

Compound name	7	8
Chemical formula	C <sub>4</sub> H <sub>18</sub> Ag <sub>6</sub> N <sub>6</sub> O <sub>19</sub> P <sub>4</sub>	C <sub>2</sub> H <sub>8</sub> Ag <sub>2</sub> CuN <sub>4</sub> O <sub>12</sub> P <sub>2</sub>
Formula weight	1225.34	621.34
Crystal system	Monoclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>T</i> (K)	213(2)	213(2)
<i>a</i> (Å)	29.506(13)	5.0294(8)
<i>b</i> (Å)	5.442(2)	7.8443(13)
<i>c</i> (Å)	18.591(8)	9.1189(15)
$\alpha$ (°)	90	72.110(3)
$\beta$ (°)	123.376(6)	82.240(3)
$\gamma$ (°)	90	78.176(2)
<i>V</i> (Å <sup>3</sup> )	2492.8(19)	334.10(9)
<i>Z</i>	4	1
Reflections collected	6829	1940
Independent reflections	2906	1473
Data/restraints/parameter ratio	2906/7/182	1473/0/107
Unique data ( <i>R</i> <sub>int</sub> )	0.0522	0.0122
<i>D</i> <sub>calc</sub> (mg/m <sup>3</sup> )	3.265	3.088
<i>F</i> (000)	2312	297
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0785, <i>wR</i> <sub>2</sub> = 0.2091	<i>R</i> <sub>1</sub> = 0.0272, <i>wR</i> <sub>2</sub> = 0.0705
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0625, <i>wR</i> <sub>2</sub> = 0.2030	<i>R</i> <sub>1</sub> = 0.0260, <i>wR</i> <sub>2</sub> = 0.0694
Largest difference in peak and hole (e/Å <sup>3</sup> )	2.490 and −1.917 <sup>a</sup>	0.933 and −0.849

<sup>a</sup> The large electron density peaks remaining in the difference map is associated with the heavy metal center.

<sup>1</sup>H-NMR (D<sub>2</sub>O, 300 MHz, 25 °C): 3.07 ppm (d, 2 H, *J* = 12.6 Hz). <sup>31</sup>P-NMR 12.29 ppm (s).

### 3.5. Synthesis of 3, [Hg<sub>2</sub>(ampa)<sub>2</sub>](H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>)<sub>n</sub>

Ampa (0.05 g, 0.5 mmol) and Hg(NO<sub>3</sub>)<sub>2</sub> (0.13 g, 0.5 mmol) were dissolved in 3 mL of water. The reaction mixture was stirred and heated at ~100 °C for 1 h after which time the clear reaction mixture was gravity filtered. The final pH of the solution was 3. Suitable crystals for X-ray crystallography were obtained from the solution. Yield: 0.12 g, 21% based on Hg(NO<sub>3</sub>)<sub>2</sub>. M.P. 150–152 °C. IR

(KBr pellet, cm<sup>-1</sup>): 3120 (m), 2903 (s), 2618 (m), 1633 (m), 1528 (m), 1384 (s), 1165 (s), 1108 (s), 1032 (s), 931 (s), 865 (m), 827 (s), 727 (s). <sup>1</sup>H-NMR: (D<sub>2</sub>O, 300 MHz, 25 °C) 3.06 ppm (d, 2 H, *J* = 12.6 Hz), <sup>31</sup>P-NMR 11.99 ppm (s).

### 3.6. Synthesis of 4, [Pb(ampa)](NO<sub>3</sub>)<sub>n</sub>

Ampa (0.05 g, 0.5 mmol) and Pb(NO<sub>3</sub>)<sub>2</sub> (0.15 g, 0.5 mmol) were added together in an open vial containing 2 mL of water. The reaction mixture was stirred and heated at 100 °C for 1 h. After 1 h, the reaction mixture was filtered and the pH recorded, pH = 3. Suitable crystals for X-ray crystallography were obtained from the solution. Yield = 0.054 g, 18% based on Pb(NO<sub>3</sub>)<sub>2</sub>. M.P. 200–202 °C. IR (KBr pellet, cm<sup>-1</sup>): 3432 (m), 2921 (s), 2622 (m), 1774 (w), 1639 (s), 1561 (m), 1504 (m), 1382 (s), 1226 (w), 1169 (m), 1029 (s), 952 (m), 930 (w), 827 (w), 800 (w), 724 (s). <sup>1</sup>H-NMR: (D<sub>2</sub>O, 300 MHz, 25 °C) 3.03 ppm (d, 2 H, 12.6 Hz). <sup>31</sup>P-NMR 12.05 ppm (s). TGA measurements recorded minimal weight loss from 50 to 400 °C.

### 3.7. Synthesis of 5, [Ag<sub>6</sub>(ampa)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sub>n</sub>

Ampa (0.05 g, 0.5 mmol) and Ag(CF<sub>3</sub>SO<sub>3</sub>) (0.12 g, 0.5 mmol) were added together in an open vial covered with aluminum foil containing 3 mL of water. The reaction mixture was stirred and heated at 100 °C for 1 h. After 1 h, the reaction mixture was filtered. The final pH of the solution was 1. Suitable crystals for X-ray crystallography were obtained from the solution. Yield = 0.24 g, 32% based on Ag triflate. M.P. (decomp.) 140–142 °C. IR (KBr pellet, cm<sup>-1</sup>) 3451 (m), 3197 (m), 2927 (s), 2609 (w), 1635 (m), 1518 (m), 1437 (w), 1259 (s), 1171 (s), 1034 (s), 938 (w), 809 (w), 723 (m), 645 (s), 579 (m), 518 (s). <sup>1</sup>H-NMR (D<sub>2</sub>O, 300 MHz, 25 °C): 3.11 ppm, (d, 2 H, *J* = 12.9 Hz); <sup>31</sup>P-NMR 12.43 ppm (s).

### 3.8. Synthesis of 6, [Ag(ampa)<sub>2</sub>]NO<sub>3</sub>, and 7, [Ag<sub>3</sub>(ampa)<sub>2</sub>](NO<sub>3</sub>)(H<sub>2</sub>O)<sub>n</sub>

Ampa (0.1 g, 0.9 mmol) and AgNO<sub>3</sub> (0.15 g, 0.9 mmol) were added together in an open vial covered with aluminum foil containing 3 mL of water. The reaction mixture was stirred and



heated at 100 °C for 1 h. After 1 h, the colorless reaction mixture was filtered. X-ray quality crystals were obtained from slow evaporation of the solution. Yield = 0.15 g of crude product, yield of **7** = 0.09 g (M.P. 190–191 °C (decomp). IR (KBr pellet, cm<sup>-1</sup>) 2918 (s) 2628 (m), 1767 (m), 1642 (s), 1509 (m), 1348 (s), 1167 (m), 1062 (m), 1026 (m), 946 cm<sup>-1</sup> (m) 925 (m), 825 (s), 724 (s) 531 (m) 487 (m) 463 (m); <sup>1</sup>H-NMR (D<sub>2</sub>O, 300 MHz, 25 °C): 3.09 ppm, (d, 2H, J = 12.6 Hz); <sup>31</sup>P-NMR: 12.00 ppm (s).

### 3.9. Synthesis of **8**, [Ag(ampa)Cu<sub>2</sub>(NO<sub>3</sub>)<sub>n</sub>]

Ampa (0.06 g, 0.5 mmol), AgNO<sub>3</sub> (0.09 g, 0.5 mmol) and Cu(SO<sub>3</sub>CF<sub>3</sub>)<sub>2</sub> (0.1 g, 0.3 mmol) were added together in an open vial covered with aluminum foil. The reaction mixture was stirred and heated at 100 °C for 1 h. After 1 h, the reaction mixture is filtered and the solid residue discarded. From the solution (pH = 1), suitable crystals for X-ray crystallography were obtained. Yield = 0.04 g (13% based on ampa). M.P. 190–192 °C (decomp). IR (KBr pellet, cm<sup>-1</sup>): 3515 (s), 3398 (s), 3084 (s), 1610 (m), 1514 (s), 1353 (s), 1252 (s), 1175 (s), 1119 (m), 1087 (s), 1030 (s) 1256 (w), 768 (w), 732 (m), 645 (s), 581 (m), 517 (s), 467 (m). No signals were detected in the <sup>1</sup>H-NMR experiment or the <sup>31</sup>P-NMR experiment. TGA data: weight loss between 145.9 and 150.7 °C, % weight loss in this temp range = 32.5%, corresponding to the approximate loss of 2 ampa molecules (calc. 35.4%).

### 3.10. Supporting information

Crystal data has been deposited with the Cambridge Crystallographic Database, reference codes, 671351, **1**, 617259, **2**, 671258, **3**, 617256, **4**, 671263, **5**, 671262, **6**, 671260, **7** and 671261, **8**. The data can be obtained free of charge at [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)

### Acknowledgments

The Robert A Welch foundation is thanked for financial support, Grant no. P0176 (AFR) and SERC (TCU) for undergraduate support of ENZ.

### Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2008.03.023](https://doi.org/10.1016/j.jssc.2008.03.023).

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