DOI: 10.1002/ejic.200701007

A Mild Synthetic Route to Zinc, Cadmium, and Silver Polymers with (2-Pyridyl)phosphonic Acid: Synthesis and Analysis

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Keywords: Metal phosphonates / Metal polymers / X-ray crystal structures

Five new metal pyridylphosphonate polymers have been prepared, fully characterized, and their room-temperature luminescence probed. The reaction of (2-pyridyl)phosphonic acid (2pypo) with ZnX_2 (X = Br, Cl) afforded two-dimensional polymers $[Zn(X)(2pypo)]_n$ {X = Cl = (**1**), X = Br = (**2**)}, which feature cyclic 12-membered Zn–O–P cores that are interlinked by bridged oxygen atoms from the phosphonate moiety. From the room–temperature, aqueous reactions of 2pypo and the corresponding metal salts, the one-dimensional polymers $[Cd(\mu\text{-}Cl)_2(2pypo)]_n$ (**3**) and $[Hg(2pypo)]_n$ (**4**) were isolated in moderate yield. The one-dimensional structure of **3** is supported through bridging chlorides and two η2-phosphonate oxygen atoms, while **4** is a highly symmetrical polymer that exhibits pyridyl nitrogen coordination to the mercury center and uses two μ_2-oxygen atoms to polymerize. Reaction of silver triflate (CF_3SO_3Ag) with 2pypo afforded a crystalline silver polymer that displays a zig-zag arrangement of silver atoms with argentophilic interactions and that is stablized through bridged triflate and phosphonate moieties.

Introduction

In recent years the chemistry of metal phosphonates has vastly increased and is associated with many applications such as ion exchange, catalysis, and sensors.[1] Of particular interest are functionalized phosphonic acids that are relatively easily synthesized, have various coordination modes, for example, dative bonds or hydrogen-bonding, and that have potential for aromatic stacking (Figure 1). A further advantage of these ligands is their tendency to induce polymerization as a result of the strong interaction of the phosphonate group with the metal ion. This acts as an efficient building block for the self-assembly of one-, two-, and three-dimensional polymeric structures.[2] The phosphonic acid group can also be readily deprotonated to form anionic ligands that can coordinate to metal centers and compensate for charge. Much of the original work centered around four valence metal atoms that were stable in octahedral environments,[3] but recently this has been extended to divalent and trivalent elements,[4] with unique layered structures evolving through chelated- or bridged-phosphonate linkages.

The recent publication of work by Clearfield et al. that uses (4-pyridyl)phosphonic acid[5] and earlier work by Foxman and co-workers that uses both (3- and 4-pyridyl)phosphonic acids[6] to form polymeric frameworks of zinc, cobalt, manganese, and nickel have prompted us to report our related investigations in this area. We were particularly interested in the synthesis and investigation of thermally stable, crystalline, d^{10} metal frameworks prepared from mild solution syntheses. (2-Pyridyl)phosphonic acid (2pypo) has been less-widely explored relative to other substituted derivatives, as it was thought that the small bite angle associated with the 2-pyridyl substitution limits the ability of the ligand to bridge, and rather than obtaining diverse frameworks, discrete structures would be formed. Despite these limitations Zheng et al. have demonstrated the versatility of 2pypo in the preparation multidimensional polymers.[7]

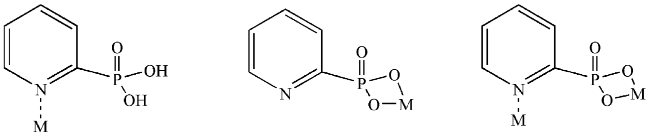

Figure 1. Various coordination modes of (2-pyridyl)phosphonic acid.

Results and Discussion

The reaction of (2-pyridyl)phosphonic acid (2pypo) with ZnX_2 (X = Cl, Br), $CdCl_2$, $Hg(NO_3)_2$, and $Ag(SO_3CF_3)$ afford polymeric structures with varying structural motifs that range from interlinked cyclic cores of the zinc halide polymers, a highly symmetrical one-dimensional mercury polymer, and a complex two-dimensional silver triflate polymer with silver–silver interactions.

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Syntheses

Polymers **1**–**4** were obtained during our systematic investigations of pyridylphosphonic acids with metal salts. Traditional methods for polymer formation employ two general routes: high-temperature solvothermal syntheses or room-temperature slow diffusion techniques.[1–6] In contrast to these methods, we wished to examine the outcome of reactions performed under aqueous conditions at room temperature or with gentle heating, in order to obtain crystalline products from a reproducible, scalable synthesis to enable further chemical exploration.

Discussion of Polymers 1 and 2

The reactions of zinc(II) chloride and bromide under aqueous conditions in a 1:1 ratio afforded two-dimensional polymers (Scheme 1).

The network structures of zinc chloride and bromide are essentially similar, although they crystallize in different space groups: the zinc chloride polymer **1** crystallizes in the monoclinic space group *P*2(1)/*c*, while the equivalent reaction with bromide affords colorless, crystalline needles that are orthorhombic, space group *Pbca*. The asymmetric unit and polymeric form of the zinc chloride reaction product are depicted in Figure 2.

The asymmetric unit of both **1** and **2** contains one zinc atom, a pyridylphosphonate molecule, and one halide atom. The zinc atoms have distorted tetrahedral geometry, and each coordination site is occupied by an oxygen atom. The three oxygen atoms arise from the phosphonate moiety and bridge the zinc centers. It is difficult to determine from X-ray analysis the protonation of the phosphonate oxygen atoms; however, from the electron density difference map the pyridyl nitrogen atom is protonated, so for charge balance, it is likely that the phosphonate group of the ligand is deprotonated. The hydrogen atom attached to the pyridyl nitrogen atom is involved in hydrogen bonding to O1 of the phosphonate group, the distance between the two atoms (O and H) is 1.935 Å. The N(H)–O distance of 1.961 Å and a N1–O1 distance of 2.754 Å also promotes hydrogen bonding. No free water molecules are observed in the lattice of the solid-state material. The zinc–oxygen distances (in Å) are between 1.923(2) and 1.9804(19) Å for **1**, and 1.949(4) and 1.981(4) Å for **2**; these values are within the range of comparable Zn–O bonds.[8] Overall, the polymers are made up of 12-membered cyclic systems comprising zinc, oxygen, and phosphorus atoms surrounded by flanking halide and pyridyl groups (Figure 3). This type of ring motif is common for zinc phosphates and phosphonates.[6] Around the cyclic core, the pyridyl groups adopt a "*cis*-type" geometry separated by a distance of 4.930 Å between parallel rings and a Zn–Zn distance of 5.166 Å. Polymer **2** has a py–py separation of 4.738 Å and a Zn–Zn distance of 4.502 Å. A terminal halide is present in both polymers **1** and **2**, which limits polymer dimensionality.

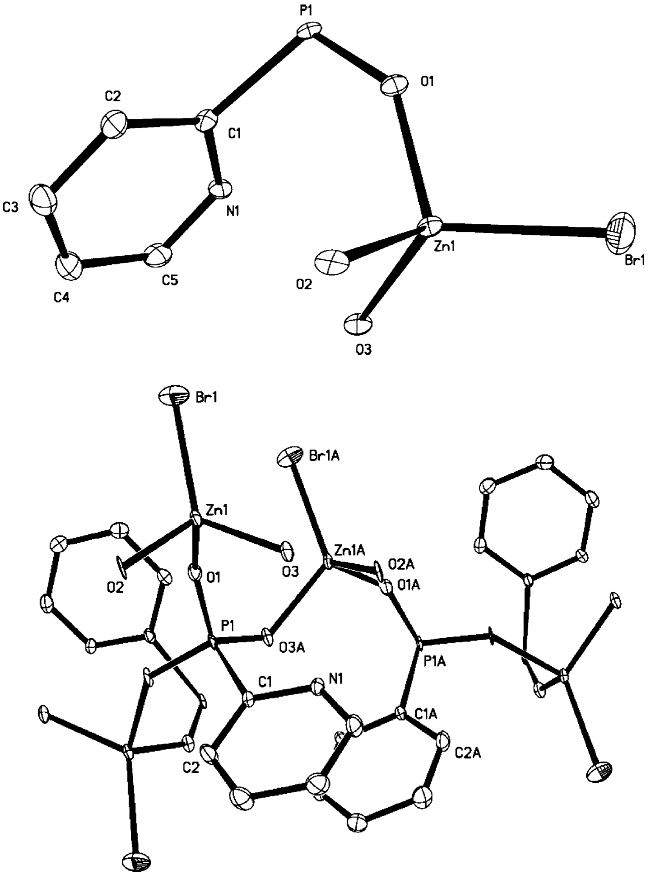
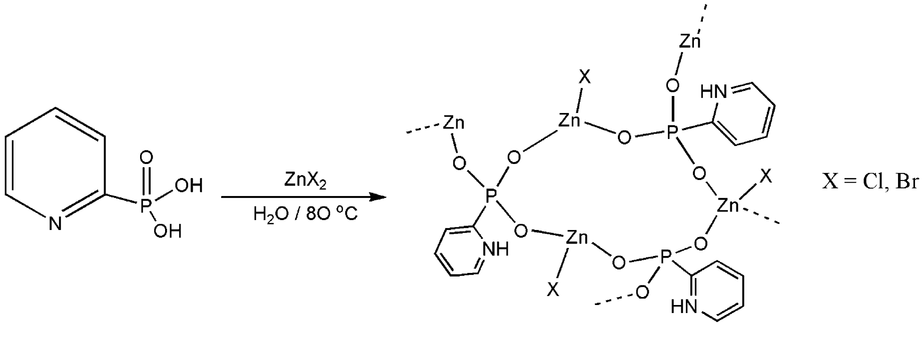


Figure 2. X-ray crystal structure of the asymmetric unit and polymeric form of $[ZnCl(2pypo)]_n$, thermal ellipsoids are at 30% and hydrogen atoms are omitted for clarity.



Scheme 1. Synthesis of polymers **1** and **2**.

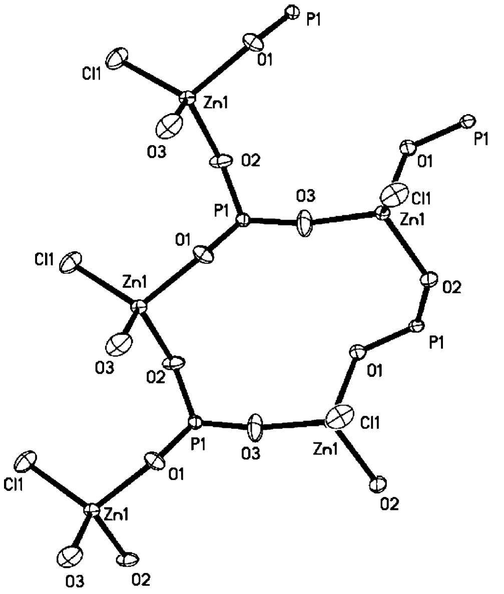


Figure 3. Crystal structure of the 12-membered cyclic core that makes up polymer **1**. Thermal ellipsoids at 50% probability, hydrogen atoms and pyridyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–O1 1.522(2), P1–O3 1.496(2), P1–O2 1.5032(19), Zn1–O1 1.9804(19), Zn1–O2 1.9487(19), Zn1–O3 1.923(2), O3–Zn1–O2 108.66(9), O3–Zn1–O1 105.29(9), O3–Zn1–Cl1 117.36(7).

The structure of polymers **1** and **2** show structural similarity with Zn[(3-pyridyl)phosphonate] bromide prepared by hydro(solvo) thermal synthesis from zinc chlorate and the hydrobromide salt of the ligand.[6] Like in polymers **1** and **2**, a cyclic core is present, although in this case, only eight atoms make up the core. Each zinc atom is doubly bridged to another zinc center by the phosphonate oxygen atoms to form a one-dimensional ladder structure along the *b* axis. Infrared data of **1** shows symmetric and asymmetric P–OH stretches at 3223.6 cm^{-1} (m), deformation at 1606.7 cm^{-1}, that are attributed to the strong hydrogen-bonding interaction with the phosphonate oxygen atoms. PO_3 stretching modes are observed between 1283.9 and 961.9 cm^{-1}, and the NH stretch is at 3109.9 cm^{-1}. The C–C and C–N stretches associated with the pyridyl ligand occur between 1525.7 and 1414.6 cm^{-1}. These values are consistent with recorded literature for systems with similar coordination modes.[9] Similar values are observed for **2**. The ^{31}P NMR spectra for both polymers display a single peak, which indicates one phosphorus environment at δ = 1.21 ppm (**1**) and at 0.40 ppm (**2**). The free ligand has a phosphorus chemical shift at δ = –3.15 ppm.[10] Polymers **1** and **2** are thermally robust, with no decomposition observed at 250 °C; however, visually (during melting point measurements), some mass loss can be detected at around 45–50 °C. TGA data were recorded on compounds **1** and **2**. Weight loss in this temperature range was found to be negligible (0.23 and 0.19%, respectively), which indicates that no free guest water molecules are present. A melting transition is observed for both polymers between 115.0–130 °C, no other changes are observed up to 400 °C.

Structure of $[Cd(\mu\text{-}Cl)_2(2pypo)]_n$ (3)

The 1:1 reaction of 2pypo in water with $CdCl_2{\cdot}2.5H_2O$ afforded a one-dimensional framework. Colorless crystals of **3** suitable for single-crystal analysis were isolated from slow evaporation of an aqueous solution at room temperature. Single-crystal structural analysis on the crystals shows that **3** crystallizes in the orthorhombic space group *Pbca*, the crystal structure of **3** is shown in Figure 4.

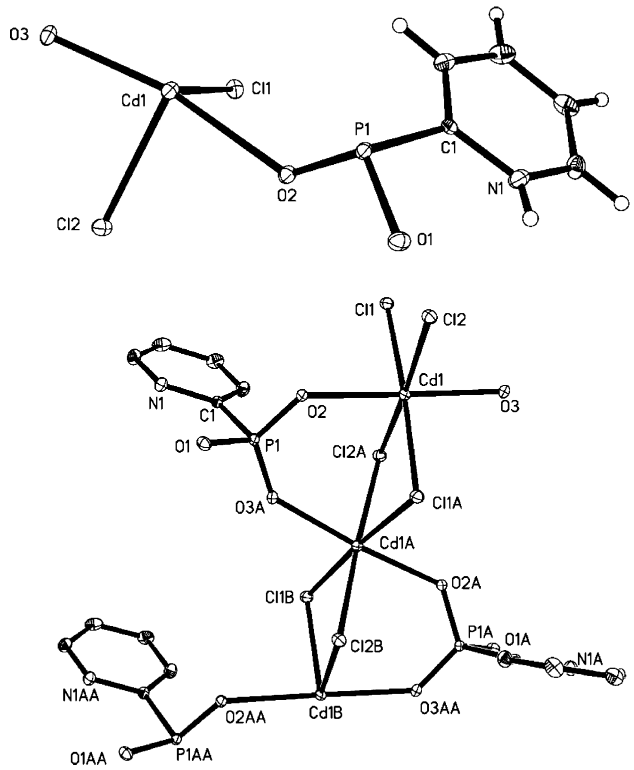


Figure 4. X-ray structural analysis of **3**, thermal ellipsoids at 30% probability and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cd1–Cl1 2.6223(15), Cd1–Cl2 2.5980(15), Cd1–O2 2.397(4), Cd1–O3 2.290(4), Cl2–Cd1–Cl1 86.43(5), Cl1–Cd1–O2 91.60(10), Cl2–Cd1–O(3) 83.07(11).

The cadmium center has slightly distorted octahedral geometry and has μ_2-oxygen and chlorine atoms adjacent to the cadmium centers. Both the chloride and oxygen bridges between the cadmium centers show small differences in their bond lengths, but correspond well to other reported values.[11] The bridged oxygen atoms are deprotonated, and this, along with the charge from the halides, indicate that the pyridyl nitrogen atom is protonated. The OH stretches are seen in the infrared spectrum, but these are considerably weaker than those observed for **1** and **2**, and arise from strong H-bonding. The distance separating the cadmium centers is 3.698 Å.[12] This is longer than the sum of the Van der Waals radii of cadmium,[13] and therefore Cd–Cd interaction is unlikely; π–π stacking is also ruled out, because the distance between the pyridyl groups is 7.388 Å and the optimal distance for π stacking is 3.904 Å.[14] The structure of **3** can be compared with that of the 3D-pillared coordination network isolated from the solvothermal reaction of cadmium chlorate with (4-pyridyl)phosphonic acid.[6] The cadmium centers are coordinated to two pyridyl nitrogen atoms and four phosphonate moieties to give an octahedral geometry around the cadmium center. The proximity of the acidic functional group and nitrogen position in (2-pyridyl)phosphonic acid appears to result in structures that have constrained geometries and limited dimensionalities. The TGA data of **3** shows no weight loss up to 400 °C, which corroborates that no guest water molecules are present.

[Hg(2Pypo)]$_n$·H_2O (4)

To extend the series, the synthesis of mercury and silver frameworks was investigated. To maintain mild experimental conditions, halide precursors that have limited aqueous solubility were replaced with water-soluble precursors: mercury nitrate, silver nitrate, and silver triflate. The stoichiometric reaction of $Hg(NO_3)_2$ with 2pypo afforded X-ray quality crystals of **4** in moderate yield at ambient temperature. The solid-state analysis of **4** (Figure 5 and Figure 6) reveals that one molecule of 2pypo and one mercury center is present in the asymmetric unit. In the lattice, there is a molecule of water, for which hydrogen atoms were located by using a low angle electron density difference map and refined by using fixed positions. The mercury center is coordinated to the nitrogen atom of the pyridyl group and oxygen atoms of the phosphonate group. The phosphonate group enables the polymer to grow as every phosphorus atom has two bridging oxygen atoms, and a terminal double-bonded oxygen atom. The mercury center has a very slightly distorted octahedral geometry, with angles as expected for this geometry: N1–Hg1–N1A 180° and N1–Hg1–O1 89.36(18)°. This geometry is depicted in Figure 5.

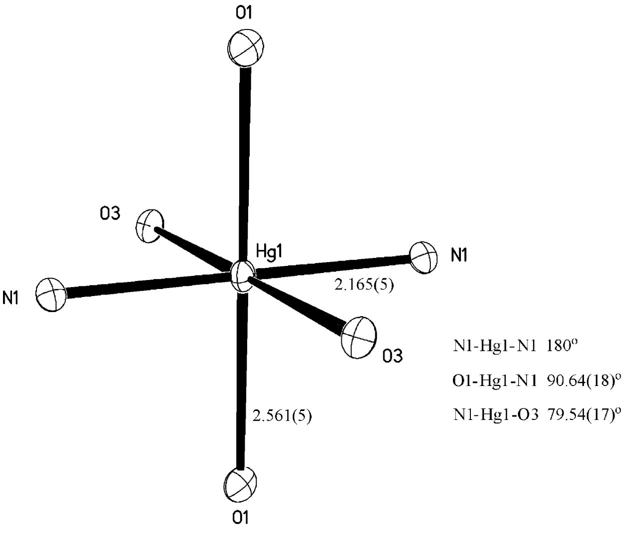
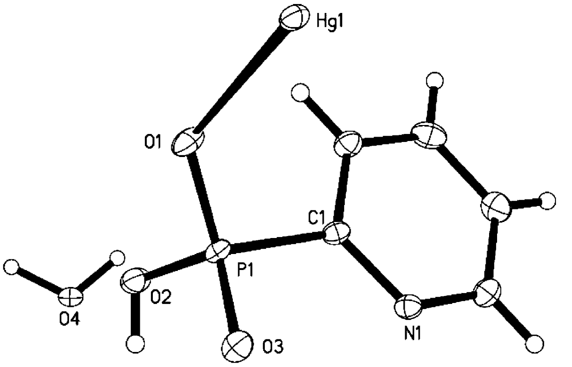


Figure 5. Diagram to display the slightly distorted octahedral geometry around the Hg center, and selected bond lengths [Å] and angles [°]. Thermal ellipsoids at 50% probability.



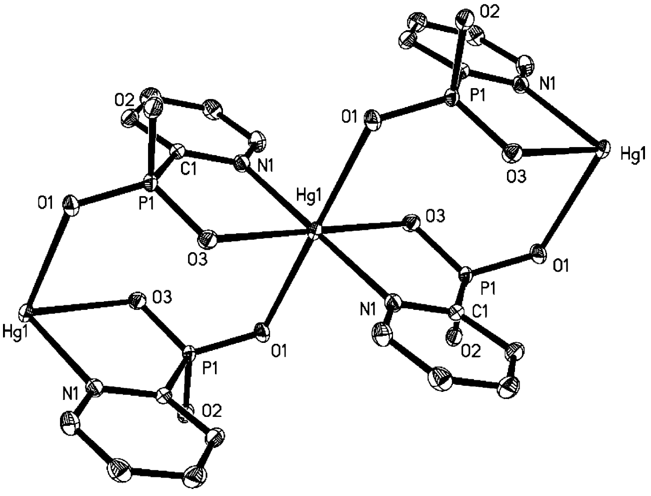


Figure 6. Structure of **4**, H atoms are omitted for clarity, thermal ellipsoids at 30% probability. Other pertinent bond angles [°] and lengths [Å]: P1–O1 1.490(5), P1–O3 1.506(6), P1–O2 1.575(6), N1–Hg1–N1A 180.0(3), N1–Hg1–O1A 90.64(18), N1A–Hg1–O3A 79.54(17), O3A–Hg1–O3 180.00(19), O1–P1–O2 108.0(3).

The Hg–O distances of 2.498(4) Å are within the range of those for other characterized Hg–O species,[15] but the Hg–N distance of 2.165(5) Å is shorter than that observed in similar Hg–py systems, and could compensate for the weak interaction between the Hg and bridged oxygen atoms.[16] A distance of 5.650 Å between the mercury centers limits any Hg–Hg interaction, since it is almost double the value of the summed Van der Waals radii (1.70 Å–2.0 Å).[17] Hydrogen bonding is present from the protonated phosphonate group to the lattice water molecule. Polymer **4** showed good thermal stability and appeared to be stable up to 300 °C (no visible decomposition). Crystalline **4** can be redissolved in water or ethanol, and heating of an aqueous solution to 100 °C for one hour reveals no structural changes (checked by solution NMR and unit cell measurements following recrystallization from the aqueous solution). The infrared spectrum exhibits strong peaks at 3540.2 and 3500.1 cm^{-1}, which corresponds to water, and at 1613.1 cm^{-1}, which is assigned to the bending vibration. In the ^{31}P solution NMR spectrum, a single phosphorus signal is observed at –0.70 ppm. The TGA data shows a weight loss of 3.12% from 120.4 °C to 136.1 °C corresponding to the loss of H_2O, which agrees with the theoretically calculated of 3.26%. Weight loss is also recorded between 194.6

and 211.1 °C corresponding to 8.1% (calculated value 12.1%), which likely occurs as a result of partial loss of the organic moiety. Decomposition occurs at 376 °C.

[Ag(triflate)(2Pypo)]$_n$ (5)

It was anticipated that the diverse coordination geometries available to silver ions that provide a wide variety of structural motifs would result in a polymeric species. However, the reaction of $AgNO_3$ with 2pypo afforded the recrystallized ligand. In order to obtain a polymeric network, other silver precursors were examined. Silver triflate (triflate = CF_3SO_3) was selected, as the $CF_3SO_3^-$ ion is considerably larger than NO_3^- and its oxygen atoms have a stronger coordinating ability than those of NO_3^-.[18] Framework **5** was isolated from the reaction of silver(I) triflate with (2-pyridyl)phosphonic acid (Figure 7).

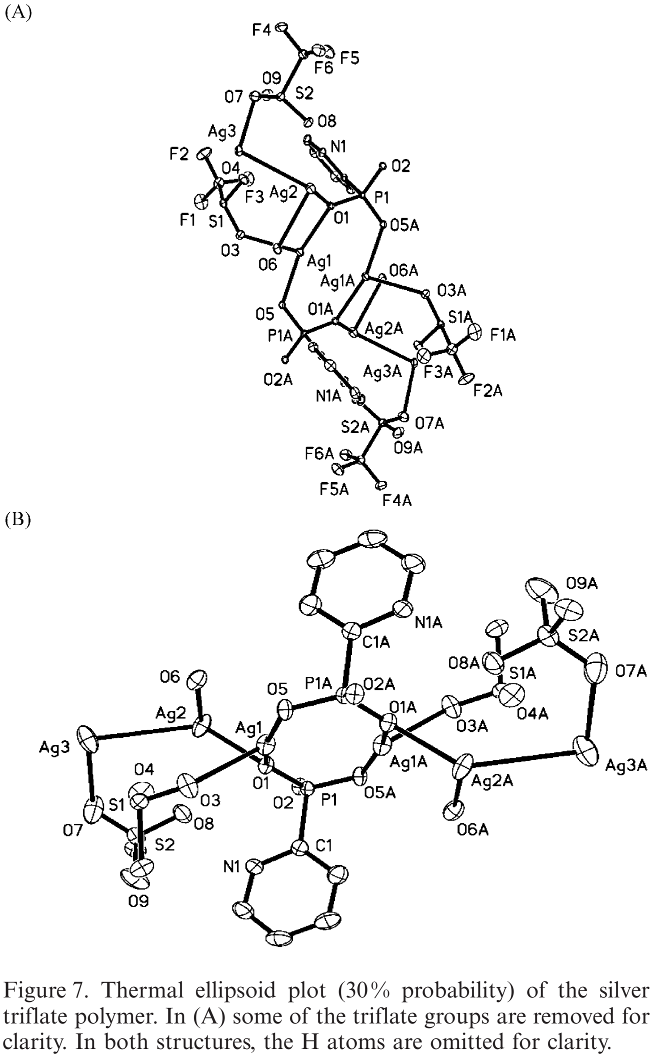


Figure 7. Thermal ellipsoid plot (30% probability) of the silver triflate polymer. In (A) some of the triflate groups are removed for clarity. In both structures, the H atoms are omitted for clarity.

In the solid state, **5** shows good photostability, although in solution slow decomposition to metallic silver occurs. Coordination of the triflate anion is not common,[19] but in polymer **5**, the triflate participates in bonding to the silver atom and also helps to stabilize the framework.[20] This occurs in conjunction with Ag–Ag interactions, which, according to Schröder,[21] helps to stabilize the polymeric network, as the energy of the Ag–Ag closed shell interaction falls into the same range as aromatic stacking. The silver–silver distances of 3.3627(5) Å and 3.0543(6) Å fall within the documented Ag–Ag interactions, which vary from 3.091–3.474 Å.[22] This is because Ag–Ag contacts are relatively weak, and this interaction is fairly small. The silver ions form a zig-zag chain in which every silver atom is five-coordinate and has a distorted trigonal-bipyrimadal geometry (Figure 8).

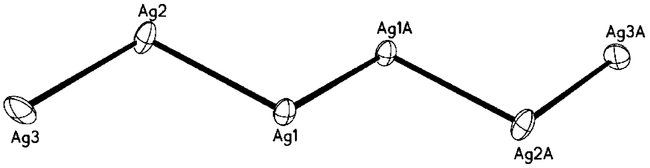


Figure 8. Zig-zag arrangement of the Ag atoms. Ag1–Ag2 3.3627(5) Å, Ag2–Ag3 3.0543(6) Å.

Examination of the repeating unit reveals three different silver environments. Ag1 is coordinated to two oxygen atoms from the phosphonate group and the oxygen atom of a triflate group. The oxygen atoms from the phosphonate bridge a second silver center, Ag2. Ag2 has a relatively short Ag–Ag distance to Ag3 [3.0543(6) Å] to which the triflate ion is attached. This short Ag–Ag interaction has a similar value to the Ag···Ag distance of 3.089(1) Å in polymeric Ag[(bpp)](CF_3SO_3)·EtOH {bpp = 1,3-bis(4-pyridyl)-propane}.[23] Thus, overall in the asymmetric unit, there are three silver centers, two triflate ions, and one phosphonate ion. The pyridyl rings form an arrangement in which the distance between them is 9.567 Å; this distance is too large for π–π stacking interactions. Selected bond lengths and angles are given in Figure 9.

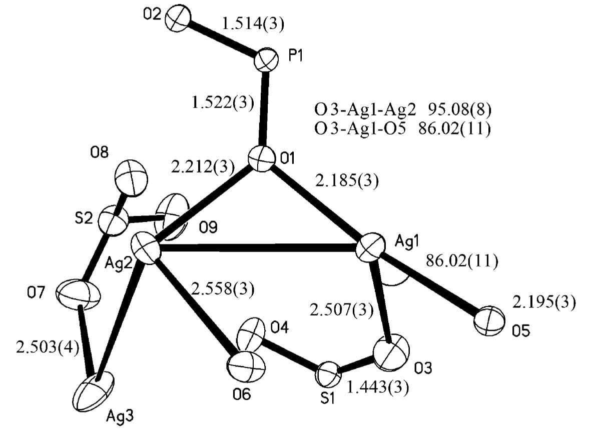


Figure 9. Selected bond lengths [Å] and angles [°] of the silver triflate polymer.

Thermal gravimetric analysis of **6** showed a melting transition that occurs at 176 °C, (m.p. recorded at 172 °C when the sample became brown). Further heating results in a weight loss of 38.7% from 226–384 °C, which is associated with the loss of the triflate and 2pypo groups (calculated value = 38.5%). No further change was observed up to 500 °C.

Luminescence Studies

Many d^{10} systems have shown promise as light-emitting diodes,[24] as the advantage of metal-containing frameworks is that their absorption and emission can be altered by changing the metal environment. To probe the potential of these systems, luminescence properties were investigated. Emission of the free ligand was recorded at excitation wavelengths 250, 275, 300, 350, and 375 nm, and emission wavelengths were recorded at 306.3 and 331 nm. At the same wavelengths, luminescence experiments of the frameworks were performed. Polymers **1**–**4** showed no luminescence at ambient temperature. Polymer **5** (silver triflate polymer), when dissolved in acetonitrile, exhibited a weak emission at 313.2 nm and shoulders associated with the ligand in its spectrum. It is thought that room-temperature luminescence is too weak to be detected and requires low-temperature measurements.

Conclusions

Several solid-state structures (**1**–**5**) were prepared under mild conditions and characterized by X-ray diffraction. (2-Pyridyl)phosphonic acid (2pypo) provides a useful ligand for the synthesis of various metal–organic frameworks. In the past, emphasis was placed on other isomers of pyridylphosphonic acid. This work demonstrates that the less common 2-isomer also provides interesting materials. Current work in our laboratory involves the preparation of other networks based on 2pypo as well as other phosphonic acid ligands. The control of the molecular structure depends both on the phosphorus-containing ligand and on the metal (and metal precursor) employed. Further results along this line of investigation will be reported in due course.

Experimental Section

Materials and Methods: 2pypo was prepared by using literature methods.[10] Other materials were purchased from Aldrich and used as received. IR spectra were recorded from KBr pellets with a FT-IR spectrometer. Thermogravimetric analysis were carried out on a Seiko 220 instrument at a heating rate of 5 °C/min. ^{1}H, ^{31}P{H} NMR spectra were recorded in solution with a Varian 300 MHz. Because of limited solubility in common deuterated solvents, no meaningful ^{13}C data could be collected. Fluorescence was recorded by using a Shimadzu 5301PC spectrofluorimeter at ambient temperature.

X-Ray Crystallography: Data collection of the compounds was performed at –60 °C on a Bruker SMART 1000, Mo-K_α (0.71073 Å) equipped with cryostream. *SAINT* was used for data reduction and cell refinement;[25] SADABS[25] was run for absorption correction on all data. Crystal structures were solved by direct methods and refined with full-matrix least-squares treatment (SHELXL).[25] Crystallographic data is summarized in Table 1. CCDC-658440, -658442, -658443, -658444, -658445, and -658445 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal Data for Compounds **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
Metal precursor used	$ZnCl_2$	$ZnBr_2$	$CdCl_2$	$Hg(NO_3)_2$	Ag(OTf)
Chemical formula	$C_5H_5ClNO_3PZn$	$C_5H_5BrNO_3PZn$	$C_5H_7CdCl_2NO_3P$	$C_{10}H_{14}HgN_2O_8P_2$	$C_7H_5Ag_3F_6NO_9PS_2$
Formula weight	258.89	303.35	343.39	552.76	779.82
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	triclinic
Space group	*P*21/*c*	*Pbca*	*Pbca*	*P*21/*n*	$P\bar{1}$
T [K]	213(2)	213(2)	213(2)	213(2)	213(2)
a [Å]	4.9295(5)	9.8688(14)	7.3883(13)	10.9312(15)	9.1388(8)
b [Å]	20.8947(19)	8.5984(12)	15.627(3)	5.6500(8)	9.5668(8)
c [Å]	8.2886(8)	20.49(3)	15.832(3)	12.3486(17)	12.2093(11)
α [°]	90	90	90	90	93.112(2)
β [°]	110.328(5)	90	90	97.920(2)	106.4150(10)
γ [°]	90	90	90	90	117.7150(10)
V [Å^3]	829.90(13)	1738.8(4)	1827.8(6)	755.39(18)	884.52(13)
Z	4	8	8	2	2
Reflections collected	4934	8393	8485	3359	5811
Independent reflections	1956	1756	1649	1348	3954
Data/restraints/parameter ratio	1953/0/113	1756/6/113	1649/0/122	1348/2/115	3954/2/266
Unique data (*R* int)	0.0369	0.0545	0.0538	0.0348	0.0185
$D_{calcd.}$ [Mg/m^3]	2.072	2.318	2.496	2.430	2.928
F(000)	516	1168	1320	524	736
R indices (all data)	$R1 = 0.0380$, $wR2 = 0.0859$	$R1 = 0.0595$, $wR2 = 0.1203$	$R1 = 0.0588$, $wR2 = 0.0735$	$R1 = 0.0704$, $wR2 = 0.1836$	$R1 = 0.0396$, $wR2 = 0.0955$
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0314$, $wR2 = 0.0806$	$R1 = 0.0420$, $wR2 = 0.1047$	$R1 = 0.0297$, $wR2 = 0.0580$	$R1 = 0.0674$, $wR2 = 0.1753$	$R1 = 0.0349$, $wR2 = 0.0910$
Largest difference in peak and hole [e Å^{-3}]	0.632 and –0.722	1.111 and –1.115	0.774 and –0.580	6.046 and –5.119[a]	2.718 and –2.781[a]

[a] The large electron density peak found in the difference map is associated with the Hg and Ag centers. Various crystals from different samples and solvents and attempts to vary crystal size all resulted in the same problem.

Synthesis of [(2pypo)ZnCl]$_n$ (1) by Reaction of ZnCl$_2$ and 2pypo: 2pypo (0.1 g, 0.63 mmol) and $ZnCl_2$ (0.09 g, 1.0 mmol) were dissolved in water (about 5 mL) in a vial and stirred at room temperature for 30 min. The initial crystals were obtained from a flask that was heated for a further 20 min at 70 °C; however, on repeating the reaction, the product was formed at room temperature. Colorless crystals suitable for X-ray diffraction were obtained by slow evaporation of the solution at room temperature. Yield: 0.067 g (41%, based on 2pypo). Melting point > 250 °C, on slow heating of the crystalline material, contraction of the solid is visible between 40–50 °C. This corresponds with results obtained by TGA (see text). IR (KBr pellets): $\tilde{\nu}$ = 3223.6 (m), 3109.9 (m), 3018.91 (m), 3008.2 (m), 2918.6 (m), 2861.6 (m), 1606.7 (s), 1525.7 (s), 1439.7 (s), 1414.6 (m), 1283.9 (m), 1169.3 (s), 1152.3 (s), 992.4 (s), 961.9 (m), 909.5 (w) cm^{-1}. $C_5H_5ClNO_3PZn$ (258.89): calcd. C 23.19, H 1.94, N 5.41; found C 23.78, H 1.89, N 5.61%. ^1H NMR (300 MHz, 25 °C, D_2O): δ = 8.03 (m, 1 H), 8.22 (m, 1 H), 8.54 (m, 1 H), 8.76 (m, 1 H) (all broad signals) ppm. $^{31}P\{H\}$ NMR (121 MHz, 25 °C, D_2O): δ = 1.2 ppm.

Synthesis of [(2pypo)ZnBr]$_n$ (2) by Reaction of 2pypo and ZnBr$_2$: 2pypo (0.10 g, 0.63 mmol) and $ZnBr_2$ (0.14 g, 0.63 mmol) were dissolved in water (about 5 mL) in a vial and stirred at room temperature for 30 min. Colorless crystals suitable for X-ray diffraction were obtained by evaporation of the solution by heating at about 100 °C. Yield: 0.15 g (81%, based on $ZnBr_2$). Melting point > 250 °C, on slow heating of the crystalline material, contraction of the solid is visible between 40–50 °C. This corresponds with results obtained by TGA (see text). IR (KBr pellets): $\tilde{\nu}$ = 3216.4 (s), 3085.3 (s), 1604.1 (s), 1523.3 (s), 1439.5 (s), 1288.2 (s), 1202.3 (s), 1108.0 (s), 1080.9 (s), 1108.0 (s), 1015.7 (s), 951.9 (s), 779.2 (s), 722.4 (s), 624.7 (m), 554.8 (s), 448.2 (m), 419.0 (m) cm^{-1}. ^1H NMR (300 MHz, 25 °C, D_2O): δ = 8.75 (d, J = 6 Hz, 1 H), 8.52 (m, 1 H), 8.20 (t, J = 7.5 Hz, 1 H), 8.01 (m, 1 H) (all broad signals) ppm. $^{31}P\{H\}$ NMR (121 MHz, 25 °C, D_2O): δ = 0.4 ppm.

Synthesis of [Cd(μ-Cl)$_2$(2pypo)]$_n$ (3) by Reaction of 2pypo and CdCl$_2$·2.5H$_2$O: 2pypo (0.1 g, 0.63 mmol) and $CdCl_2 \cdot 2.5H_2O$ (0.14 g, 0.63 mmol) were dissolved in water (5 mL) in a vial and stirred at room temperature for 15 min, followed by heating for a further 20 min at 70 °C. The solution was filtered (gravity) to remove any impurities and concentrated by heating to 100 °C for about 10 min. Colorless crystals suitable for X-ray diffraction were obtained by slow evaporation of the solution at room temperature. Yield: 0.13 g (62%). Melting point > 250 °C, on slow heating of the crystalline material, contraction of the solid is visible between 40–50 °C. IR (KBr pellets): $\tilde{\nu}$ = 3210.0 (s), 3163.2 (s), 3088.0 (s), 1595.1 (m), 1518.8 (m), 1443.3 (m), 1203.9 (s), 1153.8 (m), 1203.9 (m), 1079.9 (s), 1031.1 (s), 1009.3 (m), 946.6 (m), 873.8 (m), 816.2 (m), 763.2 (s), 718.5 (s), 562.2 (s), 531.8 (s), 495.1 (s) cm^{-1}. $C_5H_7CdCl_2NO_3P$ (343.39): calcd. C 17.49, H 2.05, N 4.08; found C 17.68, H 2.10, N 4.36%. ^1H NMR (300 MHz, 25 °C, D_2O): δ = 8.80 (d, J = 6 Hz, 1 H), 8.63 (tm, J = 8 Hz, 1 H), 8.27 (t, J = 7.5 Hz, 1 H), 8.11 (t, J = 7.5 Hz, 1 H) ppm. $^{31}P\{H\}$ NMR (121 MHz, 25 °C, D_2O): δ = –0.7 ppm.

Synthesis of [Hg(2pypo)]$_n$·H$_2$O (4) by Reaction of 2pypo and Hg(NO$_3$)$_2$: 2pypo (0.1 g, 0.62 mmol) and $Hg(NO_3)_2 \cdot H_2O$ (0.21 g, 0.64 mmol) were added to water (about 5 mL) in an open vial. The suspension was stirred at 100 °C. After 2 h, the suspension was filtered. The solid residue was discarded. From the clear solution, crystals suitable for X-ray diffraction were obtained. Melting point: >250 °C. Yield: 0.25 g [66%, based on $Hg(NO_3)_2$]. IR (KBr pellets): $\tilde{\nu}$ = 3540.2 (s), 3500.1 (s), 2925.0 (s), 2905.2 (m), 1613.0 (s), 1385.5 (s), 1013.2 (m), 928.7 (s), 770.4 (m), 732.5 (m) cm^{-1}. $C_{10}H_{14}HgN_2O_8P_2$ (552.76): calcd. C 21.72, H 2.55, N 5.07; found C 20.68, H 2.19, N 5.15. ^1H NMR (300 MHz, 25 °C, D_2O, 25 °C): δ = 8.75 (d, J = 6 Hz, 1 H), 8.50 (d, J = 6 Hz, 1 H), 8.23 (t, J = 6.8 Hz, 1 H), 8.05 (t, J = 7 Hz, 1 H) ppm. $^{31}P\{H\}$ NMR (121 MHz, 25 °C, D_2O): δ = –0.7 ppm.

Synthesis of[Ag(triflate)(2pypo)]$_n$ (5) by Reaction of 2pypo and Silver(I) Triflate: 2pypo (0.1 g, 0.63 mmol) was dissolved in water (3 mL) and added to an ethanol solution of silver(I) trifluoromethanesulfonate (0.16 g, 0.63 mmol) at room temperature, in the absence of light. The resultant mixture was stirred at room temperature for 1 h. The reaction mixture was filtered, the solution was kept, and the solid residue (some Ag) was discarded. From the aluminum foil covered solution, crystals suitable for X-ray diffraction were obtained. Melting point: decomposes at 172 °C. Yield: 0.09 g, (22.5%, based on Ag triflate). IR (KBr pellets): $\tilde{\nu}$ = 3469.7 (m), 3241.9 (w), 3173.4 (w), 3105.0 (m), 3052.6 (w), 1622.9 (s), 1454.3 (m), 1266.2 (s), 1172.0 (s), 1032.9 (s), 643.4 (s) cm^{-1}. $C_7H_5Ag_3F_6NO_9PS_2$ (779.82): calcd. C 10.78, H 0.65, N 1.8; found C 10.81, H 0.92, N 1.92. ^1H NMR (300 MHz, 25 °C, D_2O, 25 °C): δ = 8.75 (d, J = 6 Hz, 1 H), 8.42 (m, 1 H), 8.23 (t, J = 8 Hz, 1 H), 8.06 (t, J = 7.2 Hz, 1 H) ppm. $^{31}P\{H\}$ NMR (121 MHz, 25 °C, D_2O): δ = –1.1 ppm. $^{19}F\{H\}$ NMR (282 MHz, 25 °C, D_2O): δ = –79.4 ppm.

Acknowledgments

The Robert A Welch foundation is thanked for financial support, Grant No. P0176 (A. F. R.), TCU-SERC, RCAF (A. F. R.). J. L. M. acknowledges the National Institute of General Medical Sciences/NIH (1R01 GM067610) for financial support of this research.

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Received: September 18, 2007
Published Online: November 20, 2007