Hydrothermal syntheses and structures of cobalt(II) and copper(II) coordination polymers with 1-tetrazole-phenyl-4-methylphosphonate ligands.

Tiffany M. Smith Pellizzeri,^a Y.-Z. Zhang,^b Jonathan Gooch,^a Adam Lau,^a Sharde McLeish,^a
Kim R. Dunbar,^{b,*} and Jon Zubieta^{a,*}

Department of Chemistry, Syracuse University,
Syracuse, NY 13244 USA

and

Department of Chemistry, Texas A&M University,
College Station, TX 77842 USA

^a Department of Chemistry, Syracuse University;
E-mail: jazubiet@syr.edu.

^b Department of Chemistry, Texas A&M University;
E-mail: Dunbar@mail.chem.tamu.edu.

Abstract. Hydrothermal reactions of copper(II) and cobalt(II) salts with 1-tetrazole-phenyl-4-methylphosphonic acid yielded the coordination polymers $[\text{Cu}(\text{H}_2\text{O})(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4)] \cdot \text{H}_2\text{O}$ (**1**·H₂O) and $[\text{Co}(\text{H}_2\text{O})_2(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4\text{H})_2] \cdot 2\text{H}_2\text{O}$ (**2**·2H₂O). Compound **1**·H₂O is two dimensional and is constructed from chains of *trans*-corner sharing, ‘4+2’ axially distorted $\{\text{CuO}_4\text{N}_2\}$ octahedra. These chains are linked through the organic tethers of the ligands in the doubly deprotonated form $\{\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4\}^{2-}$ to propagate in two-dimensions. In contrast, compound **2**·2H₂O is one-dimensional and features $\{\text{CoO}_4\text{N}_2\}$ octahedra linked through pairs of ligands in the singly deprotonated form $\{\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4\text{H}\}^{-1}$, i.e. with the tetrazole terminus in the neutral form. The magnetic properties of compound **1**·H₂O reflect the structure where the Cu(II) ions are bridged by syn-syn phosphate and tetrazolate Cu-N-N-Cu bridges, with the former linkage likely to transfer ferromagnetic coupling whereas the latter leads to antiferromagnetic coupling. The two competing pathways lead to negligible overall coupling.

Keywords: Solid state coordination chemistry; metal-organophosphonate; mixed tetrazole/phosphonic acid ligand; cobalt(II)-tetrazole-phosphonate chain; copper(II)-tetrazolate-phosphonate network.

1. Introduction.

One approach to the design of new solid state materials exploits the principles of coordination chemistry where the geometric preferences of metal centers and appropriate multitopic ligands act as tethers provide the structural determinants. A common approach to the preparation of such organic-inorganic hybrid materials has used 4,4'-bipyridine or dicarboxylic acids as the organic spacers [1-5]. However, α , ω -alkyldiphosphonic acids provide an alternative approach to a rich coordination chemistry, often based on buttressed layer structures featuring organic and inorganic domains [6]. This strategy has allowed the development of an expansive chemistry of vanadium oxides and molybdenum oxides with diphosphonate ligands [7-27]. The structural chemistry of metal-diphosphonic acid compounds can be further expanded by introducing the positional isomers of xylyldiphosphonate ligands [28-35].

In the course of our investigations of metal-organophosphonate chemistry, a subclass of dipodal ligand types exhibiting different donor group termini, such as 1,4-carboxy-phenylphosphonic acid, $\text{H}_2\text{O}_3\text{PC}_6\text{H}_4\text{CO}_2\text{H}$ (Scheme 1), were used to prepare a family of bimetallic copper vanadate materials [26]. The incorporation of different donor groups should provide considerable structural versatility, as well as the potential for designed pillared layer materials with alternating layer compositions.

Another ligand type of particular relevance to the design of new materials is the polyazaheteroaromatic ligand, such as imidazole, pyrazole, triazole, tetrazole and their derivatives. This ligand family is characterized by a potential to bridge multiple metal sites to form polynuclear materials, as well as the ability to promote superexchange in the design of materials with unusual magnetic properties [36-51]. The ligands have been shown to be readily derivatized for applications in coordination frameworks with gas storage properties [52-56]. In recent years, the structural chemistry of mixed dipodal ligands such as pyridyltetrazole and aminophenyltetrazole has received some attention in the design of coordination polymers [57-73]. In view of the expansive chemistry of both the organophosphonates and the azolates, we sought to conflate the possibilities in a mixed dipodal ligand 1-tetrazole-phenyl-4-methylphosphonic acid, $\text{H}_2\text{O}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4\text{H}$ (**L1H₂**). In this contribution, we describe the ligand synthesis, the hydrothermal syntheses and structures of $[\text{Cu}(\text{H}_2\text{O})(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4)] \cdot \text{H}_2\text{O}$ (**1**· H_2O) and $[\text{Co}(\text{H}_2\text{O})_2(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4)_2] \cdot 2\text{H}_2\text{O}$ (**2**· $2\text{H}_2\text{O}$) along with the magnetic properties of **1**· H_2O .

2. Experimental Section

2.1 Synthetic Considerations.

All chemicals were used as obtained without further purification. Acetonitrile (99.8%), toluene (99.5%), sodium hydroxide (99.99%), triethyl phosphite (98%), cobalt(II) acetate tetrahydrate (99.999%), copper(II) chloride dihydrate (97%) and hydrofluoric acid (48 wt. % in H₂O) were all purchased from Sigma-Aldrich. Sodium azide (99%), 4-(bromomethyl) benzonitrile (98%), triethylamine·HCl (98%) and HCl (99%) were all purchased from Alfa Aesar. The synthesis of compounds **1**·H₂O and **2**·2H₂O were carried out in a 23-mL poly(tetrafluoroethylene)-lined stainless steel containers under autogeneous pressure. The pH of the solutions were measured prior to and after heating using pHydrion vivid 1-11® pH paper. Water was distilled above 3.0MΩ in-house using a Barnstead Model 525 Biopure Distilled Water Center.

2.2 Synthesis of 1,4-(CH₃CH₂)₂O₃PC₈H₇N₄ (**L1-Et₂**).

To a 250mL round-bottom flask equipped with a magnetic stir-bar were added 2.0 g of 4-(bromomethyl) benzonitrile (98%) and 30mL triethyl phosphite. The reaction mixture was allowed to reflux for 24 hours. After the reaction cooled, the reaction mixture was vacuum-distilled yielding a yellow oil. To the resulting yellow oil was added 0.64g sodium azide (9.85 mmol), 1.3554g triethylamine·HCl (9.85 mmol) and 40mL of toluene. The reaction mixture was then left to reflux for 24 hours.

After cooling the reaction mixture, an aqueous solution of NaOH (1.0 M, 50 mL) was added and the mixture was stirred for 30 minutes. The aqueous layer was separated and treated with concentrated HCl until the solution reached pH 1.0, yielding a white precipitate. The resulting solution and precipitate were placed in the refrigerator overnight and filtered the following morning to yield a white powder which was collected by filtration and dried (0.190 g, 6.3% yield), yielding 1,4-(CH₃CH₂)₂O₃PC₈H₇N₄ (**L1-Et₂**). To crystallize the product for the crystal structure determination, a small amount of the compound was dissolved in water and allowed to sit overnight to yield colorless rod-shaped crystals of **L1-Et₂**. IR (KBr pellet, cm⁻¹): 3063(w), 2987(m), 2921(m), 2856(m), 2756(m), 2625(w), 1615(m), 1566(m), 1502(s), 1441(m), 1393(m), 1235(s), 12109(s), 1194(s), 1147(w), 1052(s), 1025(s), 968(s), 902(m), 861(w), 831(w), 813(w), 776(w), 753(w), 729(w), 704(w), 558(s), 502(w), 461(w). ¹H NMR (400MHz, D₂O) δ

7.99-7.58 (2H, m), 7.59-7.51 (2H, m), 4.17-4.10 (3H, m), 3.95-3.87 (1H, m), 3.45 (1H, d), 3.19-3.11 (1H, m), 1.31-1.17 (6H, m). Crystal data for **L1-Et₂** (C₁₂H₁₇N₄O₃P): monoclinic, P2₁, a = 9.076(1) Å, b = 16.377(2) Å, c = 9.590(1) Å, β = 95.963(2)°, V = 1417.8(3) Å³, Z = 4, D_{calc} = 1.388 g cm⁻³, μ = 2.07 cm⁻¹, MoK_α radiation (λ = 0.71073 Å), R₁ = 0.0505, wR₂ = 0.1018 for 5534 reflections.

2.3 Synthesis of 1,4-H₂O₃PC₈H₅N₄ (**L1H₂**).

To a 250mL round-bottom flask equipped with a magnetic stir-bar was added 4.0 g of 1,4-(CH₃CH₂)₂O₃PC₈H₇N₄ (**L1-Et₂**) along with 100 mL of concentrated HCl. The mixture was then refluxed for 24 hours. After cooling, the HCl was distilled off to yield a white powder. Acetonitrile was added to the flask to rinse the product and it was placed in the refrigerator overnight. The resulting white powder was collected by filtration and dried in air to give 1,4-H₂O₃PC₈H₇N₄ (**L1H₂**) (3.313 g, 100% yield). Suitable crystals for structure determination were obtained by dissolving a small amount of the ligand in water and allowing it to sit overnight to yield colorless rod-shaped crystals of (**L1H₂**). IR (KBr pellet, cm⁻¹): 3049(w), 2914(m), 2851(m), 2722(m), 2638(m), 1616(m), 1570(w), 1506(m), 1446(m), 1408(w), 1261(m), 1154(s), 1132(s), 1081(s), 1021(s), 994(s), 853(m), 830(w), 719(w), 705(w), 644(w), 546(s), 496(m), 465(w). ¹H NMR (400MHz, D₂O) δ 7.83 (2H, d), 7.47 (2H, d), 3.24 (1H, s), 3.19 (1H, s). Crystal data for **L1H₂** (C₈H₉N₄O₃P): monoclinic, P2₁/n, a = 8.711(2) Å, b = 15.317(3) Å, c = 15.517(3) Å, β = 95.060(2)°, V = 2062.2(7) Å³, Z = 4, D_{calc} = 1.547 g cm⁻³, μ = 2.65 cm⁻¹, MoK_α radiation (λ = 0.71073 Å), R₁ = 0.0350, wR₂ = 0.0887 for 4206 reflections.

2.4 Synthesis of [Cu(H₂O)(HO₃PC₈H₆N₄)]·H₂O (**1·H₂O**).

A solution of copper (II) chloride dihydrate (0.115g, 0.67mmol), 1,4-H₂O₃PC₈H₅N₄ (**L1H₂**) (0.10 g, 0.42 mmol), H₂O (10mL, 556mmol) and HF (150μL, 4.35mmol) with the mole ratio of 1:0.63:829:6.5 was stirred briefly before heating to 135°C for 2 days. The initial and final pH values were 1 and 1, respectively. Blue blocks suitable for x-ray diffraction were isolated in 70% yield. IR (KBr pellet, cm⁻¹): 3304(m), 2930(m), 1617(m), 1453(m), 1432(m), 1256(m), 1153(s), 1130(s), 1087(s), 1013(w), 911(s), 846(w), 748(w), 721(m), 649(w), 544(m), 500(m). Anal. Calcd. for C₈H₁₁CuN₄O₅P: C, 28.4; H, 3.26; N, 16.6. Found: C, 28.6; H, 3.33; N, 16.2.

2.5 Synthesis of $[Co(H_2O)_2(HO_3PC_8H_7N_4)_2] \cdot 2H_2O$ (**2**· $2H_2O$).

A solution of cobalt(II) acetate tetrahydrate (0.03g, 0.12mmol), 1,4- $H_2O_3PC_8H_5N_4$ (**L1H₂**) (0.10 g, 0.42 mmol) and H_2O (10 mL, 556mmol) with the mole ratio of 1:3.5:4633 was stirred briefly before heating to 150°C for 3 days. The initial and final pH values were 5 and 1, respectively. Purple plates suitable for X-ray diffraction were isolated in 70% yield. IR (KBr pellet, cm^{-1}): 3238(m), 1619(s), 1584(w), 1509(m), 1477(w), 1419(w), 1269(w), 1140(w), 1190(s), 1160(s), 1126(s), 1067(s), 1022(w), 934(w), 895(s), 770(w), 721(w), 548(m), 486(w), 466(m). Anal. Calcd. for $C_{16}H_{24}CoN_8O_{10}P_2$: C, 31.5; H, 3.94; N, 18.4. Found: C, 31.3; H, 4.17; N, 18.3.

2.6 X-Ray Crystallography.

Crystallographic data for all compounds were collected on a Bruker KAPPA APEX DUO diffractometer containing an APEX II CCD system using Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) [74]. All data collections were taken at low temperature (90K). The data were corrected for Lorentz and polarization effects [75], and adsorption corrections were made using *SADABS* [76]. Structures were solved by direct methods. Refinements for each structure were carried out using the SHELXTL crystallographic software package [77]. Following assigning all non-hydrogen atoms, the models were refined against F^2 first using isotropic and then using anisotropic thermal displacement parameters. The hydrogen atoms were introduced in calculated positions and then refined isotropically. Neutral atom scattering coefficients along with anomalous dispersion corrections were taken from the *International Tables*, Vol. C. Images of the crystal structures were generated using CrystalMaker® [78]. Crystallographic details for the structures of **1**· H_2O and **2**· $2H_2O$ are summarized in **Table 1**.

2.7 Thermal Gravimetric Analysis.

TGA data were collected on a Perkin Elmer Pyris 1 Thermogravimetric Analyzer. Data was collected on samples that ranged between 2 and 5 mg, ramping the temperature at 10°C/minute between 25°C to 800°C.

3. Results and Discussion

3.1 Syntheses.

The bifunctional ligand **L1H₂** was prepared from the diethyl ester **L1-Et₂**. The product of the reaction of 4-(bromomethyl) benzonitrile with triethyl phosphite was treated with sodium azide and triethylamine hydrochloride. Addition of NaOH to the aqueous solution provided **L1-Et₂**, HNC₄C₆H₄CH₂PO(OEt)₂, in low yield. Treatment of **L1-Et₂** with concentrated HCl resulted in de-esterification to provide the phosphonic acid ligand **L1H₂**, HNC₄C₆H₄CH₂PO₃H₂.

The complexes of this study were prepared by the hydrothermal reactions of solutions of appropriate metal salts with **L1H₂** in water. The hydrothermal method has been shown to be ideal for the preparation of a wide variety of crystalline coordination polymers. In this case, the reaction conditions of 150 °C for 48 h under autogenous pressure resulted in the self-assembly of the cobalt product **2**·2H₂O from soluble starting materials. In the case of the copper phase **1**·H₂O, optimization required reducing the reaction temperature to 135 °C. At higher temperatures, copper was reduced to Cu(I), and only intractable materials were obtained. As noted previously [79-84], hydrothermal methods afford a number of advantages when introducing organic components into composite structures, including the reduced viscosity of water under these conditions in order to enhance diffusion processes, thus favoring extraction of solids and crystal growth, and the minimization of solubility problems that allows introduction of a variety of simple organic and inorganic precursors.

3.2 X-ray Structures.

As shown in **Figure 1**, the structure of [Cu(H₂O)(HO₃CH₂C₆H₄CN₄)]·H₂O (**1**·H₂O) is two-dimensional. The Cu(II) site displays axially distorted ‘4 + 2’ coordination through bonding to oxygen donors from two *trans* bridging aqua ligands, two oxygen donors from two *trans* phosphonate groups, and two tetrazolate nitrogen donors.

The protonation of the non-bonded phosphonate oxygen is evident in the P-O(H) distances of 1.587(2)Å, compared to an average P-O(Cu) distance of 1.508(2)Å. In this instance

the ligand is in the doubly deprotonated form, $\{\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4\}^{2-}$. Each phosphonate terminus bridges two adjacent copper sites of the aqua-bridged $\{\text{Cu}(\text{H}_2\text{O})\}_n$ chain of corner-sharing copper octahedra that provide the copper substructure. The organic tether of the ligand projects at approximately 90° with respect to the $\text{Cu}\cdots\text{Cu}$ axis of this chain. Consequently, the tetrazolate terminus of the ligand bonds to copper sites of an adjacent chain. Each tetrazolate group bridges adjacent copper sites of a chain through the N2, N3 nitrogen sites. Within a given copper chain, the copper sites share *trans* vertices through the bridging aqua ligands. Each copper site is additionally linked to adjacent copper atoms through the η^2 -bonded phosphonate and tetrazolate ligand termini.

In contrast, as shown in **Figure 2**, the structure of $[\text{Co}(\text{H}_2\text{O})_2(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4\text{H})_2] \cdot 2\text{H}_2\text{O}$ (**2**·2H₂O) is one-dimensional. The structure consists of six coordinate $\{\text{Co}(\text{II})\text{O}_4\text{N}_2\}$ sites linked through the dipodal $\{\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4\text{H}\}^{1-}$ ligands. The Co(II) sites of the chains are defined by oxygen donors from two *trans*-aqua ligands, two oxygen donors from two *trans*-phosphonate groups and two nitrogen donors from two tetrazole units.

The ligand **L1H₂** is in the monodeprotonated form $\{\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4\text{H}\}^{-1}$ with a single phosphonate oxygen deprotonated and the tetrazole terminus in the neutral, protonated form. The Co-bound oxygen donor exhibits a P-O bond length of 1.520(1)Å, while the pendant multiple P=O bond distance is 1.506(1)Å and the protonated P-O(H) bond distance is lengthened to 1.591(1)Å, unambiguously identifying the protonated site. Protonation of the phosphonate and tetrazole termini of the ligand prevents adoption of greater hapticity and the potential to bridge additional sites to generate a more complex structure or one of expanded dimensionality.

3.3 Thermal Analyses.

The TGA plot for compound **1**·H₂O displays a plateau of stability up to 98°C which is then followed by a weight loss of ~6% between 98°C and 130°C. This weight loss is assigned to the loss of the water molecule of crystallization (5.4%, calculated). Between 130°C and the limiting temperature of the instrument, 800°C, a series of several weight losses attributed to the start of the decomposition of the organic ligands are observed. The amorphous residue is most likely a copper phosphate material. The TGA plot for compound **1**·H₂O is displayed in **Figure S9**.

The TGA plot for compound **2**·2H₂O displays an initial weight loss between room temperature and 97°C of ~6% which is attributed to the loss of the water molecules of crystallization (5.9%, calculated). There is then a plateau of stability between 97°C and 195°C, followed by a series of gradual weight loss between 195°C and 800°C. During this time the initial, but not complete, decomposition of the ligands occurs. The resulting material is most likely a cobalt phosphate. The TGA plot for compound **2**·2H₂O is displayed in **Figure S10**.

3.4 Magnetic Properties.

The variable-temperature direct-current (dc) magnetic susceptibility measured in an applied field of 1 kOe for compound **1**·H₂O is shown in **Figure 3**. The $\chi_m T$ value of *ca.* 0.42 cm³ mol⁻¹ K at 300 K is slightly higher than the spin-only value (0.375 cm³ mol⁻¹ K) for one Cu²⁺ ion [85]. Upon lowering the temperature, the $\chi_m T$ product remains constant to ~15 K and then increases slightly to a value of 0.46 cm³ mol⁻¹ K at 2 K. The data obey the Curie–Weiss law ($\chi_m = C/(T-\Theta)$) with $C = 0.425$ cm³ mol⁻¹ K and $\Theta = 0.48$ K. This curve suggests only very weak ferromagnetic coupling between the neighboring Cu^{II} ions. The field dependence of the magnetization at 1.8 K is shown in **Figure 4**. The magnetization gradually saturates with the value of 1.03 N β at 50 kOe, consistent with the moment of one Cu²⁺ ion.

The magnetic susceptibility data was fitted to the uniform one-dimensional (1-D) Heisenberg chain model (**Figure 5**) with the following Hamiltonian (eq. 1):

$$H = -J \sum_{i=1}^n \hat{S}_i \cdot \hat{S}_{i+1} + \mu_B g \hat{B} \sum_i \hat{S}_i \quad (\text{eq. 1})$$

where J , μ_B , S_i , and B correspond to the exchange interaction, the Bohr magneton, the spin operator ($S = 1/2$ for Cu²⁺) and the magnetic field vector, respectively.

Thus, the molecular magnetic susceptibility is described by the well-known Fisher's formula [86] of equation 2:

$$\chi_m = \frac{N_A \mu_B^2 g^2 S(S+1)}{3k_B T} \frac{1+u}{1-u} \quad (\text{eq. 2})$$

$$\text{where } u = \coth\left(\frac{JS(S+1)}{k_B T}\right) - \left(\frac{k_B T}{JS(S+1)}\right) \quad (\text{eq. 3})$$

The best fits to the data gave $J = 0.13$ K, $g = 2.14$.

In fact, the magnetic behavior for the 1-D chain could be explained by a multinuclear ring model with the spin Hamiltonian (eq. 4) for $n = 9$:

$$H = -J \left(\sum_{i=1}^8 \hat{S}_i \cdot \hat{S}_{i+1} + \hat{S}_1 \cdot \hat{S}_9 \right) + \mu_B g \hat{B} \sum_i \hat{S}_i \quad (\text{eq. 4})$$

By using the PHI program [87], both $\chi_m T$ vs. T and M - H data was fit very well with $J = 0.20$ K and $g = 2.13$. Since in the structure, the Cu(II) ions are bridged by syn-syn phosphate and tetrazolate Cu-N-N-Cu bridges, the former linkage is likely to transfer ferromagnetic coupling [88] whereas the latter should lead to antiferromagnetic coupling [89]. Thus, it is not surprising that the two competing pathways led to negligible overall coupling. The magnetic properties of compound **1**·H₂O reflect the structure where the Cu(II) ions are bridged by syn-syn phosphate and tetrazolate Cu-N-N-Cu bridges, with the former linkage likely to transfer ferromagnetic coupling whereas the latter leads to antiferromagnetic coupling. The two competing pathways lead to negligible overall coupling.

4. Conclusions

The reactions of appropriate Cu(II) and Co(II) salts with 1-tetrazole-phenyl-4-methylphosphonic acid (H₂O₃PCH₂C₆H₄CN₄H) afforded the coordination polymers [Cu(H₂O)(HO₃PC₈H₆N₄)]·H₂O (**1**·H₂O) and [Co(H₂O)₂(HO₃PC₈H₇N₄)₂]·2H₂O (**2**·2H₂O). The one-dimensional structure of **2**·2H₂O and the two-dimensional structure of **1**·H₂O reflect in part the different protonation states of the ligand, which is present in the singly deprotonated form {HO₃PCH₂C₆H₄CN₄H}⁻¹, i.e. with the tetrazole terminus in the neutral form in **2**·2H₂O while the doubly deprotonated form {HO₃PCH₂C₆H₄CN₄}²⁻ is adopted in **1**·H₂O. The double deprotonation apparently facilitates expansion into two-dimensions by allowing the tetrazolate terminus to adopt the more common N2,N3-bridging mode.

Since the syntheses were carried out under acidic conditions, protonated forms of the ligand should be favored. Under basic conditions which force complete deprotonation to the {O₃PCH₂C₆H₄CN₄}³⁻ form of the ligand, a different structural chemistry would be expected. We

are currently investigating the chemistry of this ligand and its positional isomers (1-tetrazole-phenyl-3-methylphosphonic acid and 1-tetrazole-phenyl-2-methylphosphonic acid) under various conditions and with other transition metals and metal-oxo moieties.

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Table 1. Summary of Crystallographic Data for the Structures of This Study.

	[Cu(H ₂ O)(HO ₃ PC ₈ H ₆ N ₄)]·H ₂ O (1·H ₂ O)	[Co(H ₂ O) ₂ (HO ₃ PC ₈ H ₇ N ₄) ₂]·2H ₂ O (2·2H ₂ O)
Empirical Formula	C ₈ H ₁₁ CuN ₄ O ₅ P	C ₁₆ H ₂₄ CoN ₈ O ₁₀ P ₂
Formula Weight	337.72	609.30
Crystal System	Triclinic	Monoclinic
Space Group	P-1	P2 ₁ /n
<i>a</i> (Å)	7.4036(8)	11.1780(9)
<i>b</i> (Å)	7.5691(8)	7.5180(6)
<i>c</i> (Å)	10.8319(11)	13.2415(11)
<i>α</i> (°)	92.440(2)	90
<i>β</i> (°)	108.409(2)	91.0662(16)
<i>γ</i> (°)	91.124(2)	90
<i>V</i> (Å ³)	575.07(10)	1112.57(16)
<i>Z</i>	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.950	1.819
<i>μ</i> (mm ⁻¹)	2.062	0.991
<i>T</i> (K)	90(2)	90(2)
Wavelength	0.71073	0.71073
<i>R</i> _I ^a	0.0276	0.0227
<i>wR</i> ₂ ^b	0.0796	0.0667

$$^a RI = \Sigma |F_o| - |F_c| / \Sigma |F_o|. \quad ^b wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

Table 2. Selected bond lengths (Å) and angles (°) for and [Cu(H₂O)(HO₃PC₈H₆N₄)]·H₂O (**1**·H₂O) and [Co(H₂O)₂(HO₃PC₈H₇N₄)₂]·2H₂O (**2**·2H₂O).

[Cu(H₂O)(HO₃PC₈H₆N₄)]·H₂O (1·H₂O)			
Bond Lengths (Å)		Bond Angles (°)	
Cu1-O1	1.9189(17)	O1-Cu1-O1	180.00
Cu1-N1	2.027(2)	O1-Cu1-N1	90.94(8)
Cu2-O3	1.9176(18)	O1-Cu1-N1	89.06(8)
Cu2-N2	2.028(2)	N1-Cu1-N1	180.00
Cu1-O1	1.9190(17)	O3-Cu2-O3	180.00
Cu1-N1	2.027(2)	O3-Cu2-N2	87.98(8)
Cu2-O3	1.9176(18)	O3-Cu2-N2	92.02(8)
Cu2-N2	2.028(2)	N2-Cu-N2	180.00
P1-O1	1.5065(18)	O3-P1-O1	115.1(1)
P1-O2	1.585(18)	O1-P1-O2	108.8(1)
P1-O3	1.5091(19)	O3-P1-O2	108.6(1)
P1-C1	1.791(3)	O2-P1-C1	101.5(1)
N1-N3	1.335(3)	O3-P1-C1	110.9(1)
N3-C8	1.341(3)	O1-P1-C1	110.9(1)
N1-N2	1.309(3)		
N2-N4	1.335(3)		
N4-C8	1.338(3)		
C7-C8	1.476(3)		

[Co(H ₂ O) ₂ (HO ₃ PC ₈ H ₇ N ₄) ₂]·2H ₂ O (2·2H ₂ O)			
Bond Lengths (Å)		Bond Angles (°)	
Co1-O1	2.0779(12)	O1-Co1-O1	180.00
Co1-O2	2.1074(11)	O1-Co1-O2	19.17(5)
Co1-N1	2.1922(13)	O1-Co1-O2	88.83(5)
Co1-O1	2.0779(12)	O1-Co1-N1	88.59(5)
Co1-O2	2.1074(11)	O1-Co1-N1	91.41(5)
Co1-N1	2.1922(13)	O2-Co1-N1	89.59(5)
P1-O4	1.5058(12)	O2-Co1-N1	90.41(5)
P1-O3	1.5913(12)	N1-Co1-N1	180.00
P1-O2	1.5200(12)	O4-P1-O2	115.50(7)
P1-C1	1.8021(17)	O4-P1-O3	106.66(7)
N1-N3	1.2933(19)	O2-P1-O3	109.92(6)
N2-C8	1.331(2)	O4-P1-C1	111.36(7)
N1-N2	1.3667(19)	O2-P1-C1	109.07(7)
N3-N4	1.3414(19)	O3-P1-C1	103.64(7)
N4-C8	1.343(2)		
C7-C8	1.466(2)

Scheme 1

Figure Captions

- Figure 1.** (a) A view in the ac plane of the two-dimensional structure of $[\text{Cu}(\text{H}_2\text{O})(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN})]\cdot\text{H}_2\text{O}$ (**1**· H_2O). Color scheme: Cu, dark blue octahedra; P, yellow tetrahedra; O, red spheres; N, blue spheres; C, black spheres; H, pink spheres. The hydrogen atoms on the carbon sites have been omitted for clarity. (b) Ball-and-stick representation of the stacking of layers in the ab plane. The water molecules of crystallization are shown as stippled hollow spheres.
- Figure 2.** Mixed polyhedral and ball-and-stick representation of the one-dimensional structure of $[\text{Co}(\text{H}_2\text{O})_2(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4\text{H})_2]\cdot 2\text{H}_2\text{O}$ (**2**· $2\text{H}_2\text{O}$). Color scheme: Co, purple octahedra; P, yellow tetrahedra; O, red spheres; N, blue spheres; C, black spheres; H, pink spheres. The hydrogen atoms on the carbon sites have been omitted for clarity.
- Figure 3.** Temperature dependence of the $\chi_m T$ and χ_m product at 1 kOe for **1**· H_2O .
- Figure 4.** M vs H at 1.8 K for **1**· H_2O .
- Figure 5.** The uniform 1-D chain of **1**· H_2O .

Figure 1(a).

Figure 1(b).

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Hydrothermal syntheses and structures of cobalt(II) and copper(II) coordination polymers with 1-tetrazole-phenyl-4-methylphosphonate ligands.

Tiffany M. Smith, Y.-Z. Zhang, Jonathan Gooch, Adam Lau, Sharde McLeish, Kim R. Dunbar, and Jon Zubieta

Graphical Abstract

Hydrothermal reactions of cobalt(II) and copper(II) salts with 1-tetrazole-phenyl-4-methylphosphonic acid yield the coordination polymers $[\text{Co}(\text{H}_2\text{O})_2(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_4\text{H})_2]$ (**1**) and $[\text{Cu}(\text{H}_2\text{O})(\text{HO}_3\text{PCH}_2\text{C}_6\text{H}_4\text{CN}_4)]$ (**2**), whose structure is shown.