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Metal-organophosphonate chemistry: Hydrothermal syntheses and structures of copper(II)-xylyldiphosphonates with organonitrogen coligands

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ABSTRACT

The hydrothermal reactions of copper(II) acetate monohydrate or copper(II) chloride dihydrate with xylyl-phosphonic acid derivatives in the presence of organonitrogen coligands yielded a series of compounds of the Cu(II)/ligand/xylyl-diphosphonate system. The materials structurally characterized in the study include the parent compound $[Cu_2(H_2O)_2(1,4-O_3PC_8H_8PO_3)]$ (1); the o-phenanthroline derivatives: [Cu(H₂O)(o-Phen)(1,4-HO₃PC₈PO₃H)]·3H₂O (**2**·3H₂O), [Cu₂(H₂O)₂(1,4-O₃PC₈H₈PO₃)]·3H₂O (**3**·3H₂O), [Cu(o-phen)(1,4-HO₃PC₈H₈PO₃H)]·3H₂O (**4**·3H₂O), [Cu(o-phen)(1,2-HO₃PC₈H₈PO₃H)] (**5**), and [Cu $(o-phen)(1,3-HO_3PC_8H_8PO_3H)$ (6); the 2,2'-bipyridine derivatives: $[Cu_2(H_2O)_2(bpy)_2(1,4-HO_3PC_8H_8PO_3H)]$ $H_{2}(HO_{3}PC_{8}H_{8}PO_{3}H)] \cdot H_{2}O (\textbf{7} \cdot H_{2}O); [Cu(bpy)(1,4-HO_{3}PC_{8}H_{8}PO_{3}H)] \cdot 2H_{2}O (\textbf{8} \cdot 2H_{2}O), and [Cu(bpy)(1,3-HO_{3}PC_{8}H_{8}PO_{3}H)] \cdot 2H_{2}O (\textbf{8} \cdot 2H_{2}O), and [Cu(bpy)(1,3-HO_{3}PC_{8}H_{8}O_{3}H)] \cdot 2H_{2}O (\textbf{8} \cdot 2H_{2}O), and [Cu(bpy)(1,3-HO_{3}PC_{8}H_{8}O_{3}H_{8}O_{8}H_{8}O$ $HO_3PC_8H_8PO_3H)$] (9); the tetra-2-pyridylpyrazine materials: $[Cu_2(H_2O)_2(tpypyz)(1,4-HO_3PC_8H_8PO_3H)_2$ $\cdot (1,4-H_2O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O (\textbf{10} \cdot (H_{62}O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O), \\ [Cu_2(tpypyz)(1,2-HO_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O (H_{62}O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O) + (H_{62}O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O (H_{62}O_3PC_8H_8O_3H_2)_2 \cdot 2H_2O (H_{$ $(11.2H_2O)$, and $[Cu_4Cl_4(tpypyz)_2(1.4-H_2O_3PC_8H_8PO_3H)_2]Cl_2H_2O_3PC_8H_8O_3H_2O_1(12.H_2O_3PC_8H_8O_3H_2O_1)_2]Cl_2H_2O_3PC_8H_8O_3H_2O_1(12.H_2O_3PC_8H_8O_3H_2O_1)_2]Cl_2H_2O_3PC_8H_8O_3H_2O_1(12.H_2O_3PC_8H_8O_3H_2O_1)_2]Cl_2H_2O_3PC_8H_8O_3H_2O_1(12.H_2O_3PC_8H_8O_3H_2O_1)_2]Cl_2H_2O_3PC_8H_8O_3H_2O_1(12.H_2O_3PC_8H_8O_3H_2O_1)_2]Cl_2H_2O_2PC_8H_8O_3H_2O_1(12.H_2O_3PC_8H_8O_3H_2O_1)_2]Cl_2H_2O_3PC_8H_8O_3H_2O_1(12.H_2O_3PC_8H_8O_3H_2O_1)_2]Cl_2H_2O_3PC_8H_8O_3H_2O_1(12.H_2O_3PC_8H_8O_3H_2O_1)_2]Cl_2H_2O_2PC_8H_8O_3H_2O_1(12.H_2O_3PC_8H_8O_3H_2O_1)_2]Cl_2H_2O_2PC_8H_8O_3H_2O_1(12.H_2O_1O_1)_2]Cl_2H_2O_2PC_8H_8O_1)_2]Cl_2H_2O_2PC_8H_8O_2H_2O_1)_2]Cl_2H_2O_2PC_8H_8O_1)_2]Cl_2H_2O_2PC_8H_8O_1)_2$ Cl_2H_2O_2PC_8H_8O_2)_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2)_2Cl_2H_8O_2Cl_2H_8O_2Cl_2H_8O_2)Cl_2H_8O_2Cl_ $H_2 \cdot 8H_2O$); and the di-2,2'-pyridylamine compound [Cu(2,2dpy)(HO_3PC_8H_8PO_3H)] (13). The role of the coligand in modifying the overall dimensionality of the ultimate products is apparent. Rather than observing the common pillared layer frameworks characteristic of metal-diphosphonate materials, the o-phenthroline derivatives, compounds 4 and 5 are two-dimensional, 3 and 6 are one-dimensional and 2 is molecular. For the 2,2'-bipyridyl analogues, 8 is two-dimensional while 9 is one-dimensional and 7 is molecular. Similarly, the tetra-2-pyridylpyrazine derivatives provide a one-dimensional material 10 and two molecular species 11 and 12.

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1. Introduction

Since the first reports of layered zirconium phenylphosphonate in the 1970s [1,2], soon followed by the seminal work of Clearfield, Bujoli, and Mallouk [3–9], metal phosphonate chemistry has emerged in a vast literature detailing an unusual compositional range and structural diversity [10,11]. The structural chemistry reveals three-dimensional open frameworks [12–14], pillared layer materials [15–18], molecular phosphonate clusters and structures incorporating organoimine templates or structure-directing units [19–25].

A notable characteristic of the chemistry of metal-organodiphosphonate materials is that both the length and chemical identity of the organic tethering group can profoundly influence the overall structure. In our own work, we have noted that the oxovanadium diphosphonates of the general class $[V_2O_2(H_2O)_x {O_3P(CH_2)_nPO_3}] \cdot xH_2O$ exhibit three structure types depending on the tether length *n* [26]. However, the structures of the oxovanadates of the aromatic diphosphonates are quite distinct from those of their aliphatic counterparts [27]. Similar structural variations have also been observed for the oxomolybdate-organodiphosphonate structures [28].

Copper diphosphonates are significant subclass of metal-organodiphosphonate materials that have been designed with both aliphatic [29,30] and aromatic [31–34] linkers between the ligating groups. While three dimensional "pillared layers" and other three-dimensional frameworks are the rule for these materials, the detailed connectivities within the Cu–P–O inorganic layers may exhibit considerable variability. Furthermore, the structural chemistry of copper-organodiphosphonates can be readily expanded by introducing nitrogen-donor coligands [35–40] or by exploiting the copper-diphosphonate moiety in the construction of bimetallic oxide hybrid materials [41–46]. Encouraged by the of-





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ten unique structural chemistry of the parent copper-aromaticdiphosphonates, we recently reported on a study of the chemistry of the Cu/ligand/(phenyl diphosphonate) system (where ligand = 2,2 bipyridine (bpy), o-phenanthroline (phen) and 2,2':6,2"-terpyridine (terpy)) [47]. In an attempt to expand on these results, we have undertaken an examination of structural chemistry of the Cu(II)/ligand/xylyl-diphosphonate system in order to assess the structural consequences of introducing the more flexible xylyl-backbone in place of the rigid phenyl linker and of variations in the relative positions of the -CH₂PO₃²⁻ groups on the ring. In this study, we present the structures of the parent compound $[Cu_2(H_2O)_2(1,4-O_3PC_8H_8PO_3)]$ (1); the *o*-phenanthroline derivatives: $[Cu(H_2O)(o-phen)(1,4-HO_3PC_8H_8PO_3H)]\cdot 3H_2O$ $(2\cdot 3H_2O)$, $[Cu_2(H_2O)_2(1,4-O_3PC_8H_8PO_3)]\cdot 3H_2O$ $(3\cdot 3H_2O)$, $[Cu(0-1)]\cdot 3H_2O$ phen)(1,4-HO₃PC₈H₈PO₃H)]·3H₂O (4·3H₂O), [Cu(o-phen)(1,2-HO₃) $PC_8H_8PO_3H$] (5), and $[Cu(o-phen)(1,3-HO_3PC_8H_8PO_3H)]$ (6); the 2,2'-dipyridine derivatives: [Cu₂(H₂O)₂(bpy)₂(1,4-HO₃PC₈H₈PO₃ $H_2_2(HO_3PC_8H_8PO_3H)$]· H_2O (**7**· H_2O); [Cu(bpy)(1,4-HO_3PC_8H_8PO_3)]· H_2O (**7**· H_2O)]· H_2O (**7**· H_2O); [Cu(bpy)(1,4-HO_3PC_8H_8PO_3)]· H_2O (**7**· H_2O)]· H_2O (H)]·2H₂O (8·2H₂O), and [Cu(bpy)(1,3-HO₃PC₈H₈PO₃H)] (9); the tetra-2-pyridinylpyrazine materials: [Cu₂(H₂O)₂(tpypyz)(1,4-HO₃PC₈ $H_8PO_3H_2$]·(1,4- $H_2O_3PC_8H_8PO_3H_2$)₂·2 H_2O_1 (10·($H_2O_3PC_8H_8PO_3H_2$)₂- $\cdot 2H_2O$), $[Cu_2(tpypyz)(1,2-HO_3PC_8H_8PO_3H)_2]\cdot 2H_2O$ (**11** $\cdot 2H_2O$), and $[Cu_4Cl_4(tpypyz)_2(1,4-H_2O_3PC_8H_8PO_3H)_2]Cl_2H_2O_3PC_8H_8O_3H_2BH_2O_3H_3O_3H_2O_3H_3O_3H_2O_3H_3O_3H_2O_3H_3O_3H_2O_3H_3O_3H_2O_3H_3O_3$ $(12 \cdot H_2O_3PC_8H_8O_3H_2 \cdot 8H_2O)$; and the di-2,2'-pyridylamine compound [Cu(2,2dpy) (HO₃PC₈H₈PO₃H)] (**13**).

2. Experimental

2.1. General procedures

All chemicals were used as obtained without further purification with the exception of *p*-xylene diphosphonic acid, *ortho*-xylene diphosphonic acid and *meta*-xylene diphosphonic acid which were synthesized in a similar fashion to the method published in literature [30] using their respective dibromide starting materials. Copper(II) acetate monohydrate (98%), copper(II) chloride dihydrate (97%), sodium orthovanadate (99.98%), 2,2'-bipyridine (99%), 1,10 phenanthroline (99%), tetra-2-pyridinylpyrazine (97%), 2,2'dipyridylamine (99%), sodium hydroxide (99.99%), and hydrofluoric acid (48 wt.% in H₂O) were all purchased from Sigma-Aldrich. All syntheses were carried out in 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 $3.0 \text{ M}\Omega$ in-house using a Barnstead Model 525 Biopure Distilled Water Center.

2.2. Synthesis of $Cu_2(H_2O)_2(O_3PC_8H_8PO_3)$ (1)

A solution of copper(II) chloride dihydrate (0.0714 g, 0.42 mmol), 1,10 phenanthroline (0.0392 g, 0.22 mmol), *p*-xylenediphosphonic acid (0.080 g, 0.30 mmol), H₂O (10 mL, 556 mmol) and HF (500 μ L, 14.5 mmol) with the mole ratio of 1:0.52:0.71:1324:34.5 was stirred briefly before heating to 100 °C for 48 h. The initial and final pH values were 1 and 1, respectively. Blue-green blocks suitable for X-ray diffraction were isolated in 20% yield. IR (KBr pellet, cm⁻¹): 3232(m), 3055(m), 1560(m), 1509(m), 1409(w), 1256(w), 1141(w), 1105(m), 1042(s), 984(s), 857(s), 510(s), 512(s). *Anal.* Calc. for C₄H₆CuO₄P: C, 22.6; H, 2.82; Found: C, 22.5; H, 2.93%.

2.3. Synthesis of $Cu(H_2O)(ophen)(HO_3PC_8H_8O_3H) \cdot 3H_2O(2 \cdot 3H_2O)$

A solution of copper(II) chloride dihydrate (0.0714 g, 0.42 mmol), 1,10 phenanthroline (0.0392 g, 0.22 mmol), *p*-xylene-

diphosphonic acid (0.080 g, 0.30 mmol), and H₂O (10 mL, 556 mmol) with the mole ratio of 1:0.52:0.71:1324 was stirred briefly before heating to 120 °C for 48 h. The initial and final pH values were 1 and 1, respectively. Blue blocks suitable for X-ray diffraction were isolated in 30% yield. IR (KBr pellet, cm⁻¹): 3568(w), 3483(m), 3150(m), 3084(m), 2368(w), 2344(w), 1654(m), 1584(w), 1517(w), 1430(m), 1265(s), 1197(w), 1157(s), 1106(s), 1045(s), 940(s), 887(S), 852(m), 724(m), 550(s, 475(w). *Anal.* Calc. for C₄₀H₅₂Cu₂N₄O₂₀P₄: C, 41.4; H, 4.48; N, 4.83. Found: C, 41.5; H, 4.35; N, 68%.

2.4. Synthesis of $Cu_2(H_2O)_2(ophen)_2(O_3PC_8H_8PO_3) \cdot 3H_2O$ (3.3H₂O)

A solution of copper(II) chloride dihydrate (0.0714 g, 0.42 mmol), 1,10 phenanthroline (0.0392 g, 0.22 mmol), *p*-xylene-diphosphonic acid (0.080 g, 0.30 mmol), H₂O (10 mL, 556 mmol) and 6 M NaOH (200 μ L, 1.2 mmol) with the mole ratio of 1:0.52:0.71:1324:2.9 was stirred briefly before heating to 120 °C for 48 h. The initial and final pH values were 6 and 5, respectively. Blue rods suitable for X-ray diffraction were isolated in 5% yield. IR (KBr pellet, cm⁻¹): 3496(m), 3366(m), 3253(m), 3078(m), 3055(m), 3008(m), 1642(m), 1625(m), 1580(w), 1510(m), 1427(s), 1152(s), 1150(s), 1097(s), 1046(s), 1010(s), 920(s), 858(s), 788(m), 737(w), 722(s), 570(s). Anal. Calc. for C₁₆H₂₀CuN₂O₇P: C, 43.0; H, 4.51; N, 6.27. Found: C, 42.6; H, 4.27; N, 6.33%.

2.5. Synthesis of Cu(ophen)(HO₃PC₈H₈PO₃H) \cdot 3H₂O (**4** \cdot 3H₂O)

A solution of copper(II) chloride dihydrate (0.0714 g, 0.42 mmol), 1,10 phenanthroline (0.0392 g, 0.22 mmol), *p*-xylenediphosphonic acid (0.080 g, 0.30 mmol), and H₂O (10 mL, 556 mmol) with the mole ratio of 1:0.52:0.71:1324 was stirred briefly before heating to 150 °C for 48 h. The initial and final pH values were 1 and 1, respectively. Blue blocks suitable for X-ray diffraction were isolated in 50% yield. IR (KBr pellet, cm⁻¹): 3239(m), 3056(m), 1654(w), 1583(w), 1428(m), 1410(m), 1257(m), 1120(s), 1105(s), 1105(s), 1046(s), 950(s), 854(s), 724(s), 562(s). *Anal.* Calc. for C₂₀H₂₄CuN₂O₉P₂: C, 42.7; H, 4.27; N, 4.98. Found: C, 42.6; H, 4.19; N, 5.11.

2.6. Synthesis of $[Cu(ophen)(HO_3PC_8H_8PO_3H)]$ (5)

A solution of copper(II) chloride dihydrate (0.0714 g, 0.42 mmol), 1,10 phenanthroline (0.0392 g, 0.22 mmol), *o*-xylene-diphosphonic acid (0.080 g, 0.30 mmol), and H₂O (5 mL, 278 mmol) with the mole ratio of 1:0.52:0.71:662 was stirred briefly before heating to 135 °C for 48 h. The initial and final pH values were 2 and 1, respectively. Blue blocks suitable for X-ray diffraction were isolated in 80% yield. IR (KBr pellet, cm⁻¹): $\tilde{\nu}$ = 3214(m), 3054(m), 1702(w), 1583(m), 1422(s), 1134(w), 1107(s), 1065(s), 1027(s), 941(s), 872(s), 851(s), 788(s), 722(s), 587(s), 543(s), 521(s). Anal. Calc. for C₂₀H₁₈CuN₂O₆P₂: C, 47.3; H, 3.54; N, 5.51. Found: C, 47.0; H, 3.24; N, 5.40%.

2.7. Synthesis of $[Cu(ophen)(HO_3PC_8H_8PO_3H)]$ (6)

A solution of copper(II) chloride dihydrate (0.0714 g, 0.42 mmol), 1,10 phenanthroline (0.0392 g, 0.22 mmol), *m*-xy-lene-diphosphonic acid (0.080 g, 0.30 mmol), and H₂O (10 mL, 556 mmol) with the mole ratio of 1:0.52:0.71:1324 was stirred briefly before heating to 120 °C for 72 h. The initial and final pH values were 1 and 1, respectively. Green blocks suitable for X-ray diffraction were isolated in 85% yield. IR (KBr pellet, cm⁻¹): 3429(w), 3064(w), 2909(w), 2366(w), 2344(w), 1605(w), 1584(w), 1519(w), 1488(w), 1429(m), 1296(w), 1225(m),

1161(s), 1137(s), 1107(m). *Anal.* Calcd. C₂₀H₁₈CuN₂O₆P₂: C, 47.3; H, 3.54; N, 5.51. Found C, 47.2; H, 3.46; N, 5.44%.

2.8. Synthesis of $Cu_2(H_2O)_2(bpy)_2(HO_3PC_8H_8PO_3H_2)_2$ $(HO_3PC_8H_8PO_3H)\cdot H_2O$ (**7**·H₂O)

A solution of copper(II) acetate monohydrate (0.0634 g, 0.32 mmol), 2,2'bipyridine (0.034 g, 0.22 mmol), *p*-xylene-diphosphonic acid (0.080 g, 0.30 mmol), H₂O (10 mL, 556 mmol) and HF (500 μ L, 14.5 mmol) with the mole ratio of 1:0.69:0.94:1738:45 was stirred briefly before heating to 120 °C for 72 h. The initial and final pH values were 1 and 1, respectively. Blue blocks suitable for X-ray diffraction were isolated in 90% yield. IR (KBr pellet, cm⁻¹): 3409(s), 3092(m), 2902(m), 2344(w), 1663(w), 1607(s), 1569(w), 1473(w), 1446(m), 1300(s), 1104(s), 1097(m), 1059(m), 856(m), 768(m), 728(m), 562(s), 475(m). Anal. Calc. for C₂₂H₂₈₋CuN₂O₁₁P₃: C, 40.5; H, 4.32; N, 4.29. Found: C, 40.4; H, 4.19; N, 4.16%.

2.9. Synthesis of $Cu(bpy)(HO_3PC_8H_8PO_3H)\cdot 2H_2O$ (8.2H₂O)

A solution of copper(II) acetate monohydrate (0.0634 g, 0.32 mmol), sodium orthovanadate (0.058 g, 0.32 mmol), 2,2' bipyridine (0.034 g, 0.22 mmol), *p*-xylene-diphosphonic acid (0.080 g, 0.30 mmol), H₂O (10 mL, 556 mmol) and HF (500 μ L, 14.5 mmol) with the mole ratio of 1:1:0.69:0.94:1738:45 was stirred briefly before heating to 120 °C for 72 h. The initial and final pH values were 1 and 1, respectively. Blue blocks suitable for X-ray diffraction were isolated in 90% yield. IR (KBr pellet, cm⁻¹): 3447(w), 3150(m), 3090(w), 2902(w), 2361(s), 2342(s), 1602(s), 1560(w), 1510(w), 1444(s), 1251(s), 1203(s), 1056(s), 1010(s), 942(s), 857(m), 769(s), 729(m), 640(m), 563(s), 487(m). Anal. Calc. for C₁₈H₂₂CuN₂O₈P₂: C, 41.5; H, 4.23; N, 5.39. Found: C, 41.8; H, 4.44; N, 5.1%.

2.10. Synthesis of $[Cu(bpy)(HO_3PC_8H_8PO_3H)]$ (9)

A solution of copper(II) chloride dihydrate (0.0714 g, 0.42 mmol), 2,2′ bipyridine (0.040 g, 0.26 mmol), *m*-xylenediphosphonic acid (0.080 g, 0.30 mmol), and H₂O (10 mL, 556 mmol) with the mole ratio of 1:0.62:0.71:1324 was stirred briefly before heating to 120 °C for 72 h. The initial and final pH values were 1 and 1, respectively. Green plates suitable for X-ray diffraction were isolated in 5% yield. IR (KBr pellet, cm⁻¹): 3448(s), 2951(m), 2919(m), 1475(w), 1458(w), 1226(m), 1120 (s), 1065(w), 1031(w), 939(m), 905(m), 779(m), 704(m), 518(m). *Anal.* Calc. for C₁₈H₁₈CuN₂O₆P₂: C, 44.6; H, 3.72; N, 5.39. Found: C, 44.8; H, 3.44; N, 5.81%.

2.11. Synthesis of $[Cu_2(H_2O)_2(tpypyz)(HO_3PC_8H_8PO_3H)_2] \cdot (H_2O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O$ (**10** · $(H_2O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O$) and $[Cu_4(Cl)_4(tpypyz)_2(H_2O_3PC_8H_8PO_3H)_2] Cl_2 \cdot H_2O_3PC_8H_8O_3H_2 \cdot 8H_2O$ (**12** · $H_2O_3PC_8H_8O_3H_2 \cdot 8H_2O$)

A solution of copper(II) chloride dihydrate (0.0714 g, 0.42 mmol), tetra-2-pyridinylpyrazine (0.085 g, 0.22 mmol), *p*-xy-lene-diphosphonic acid (0.080 g, 0.30 mmol), and H₂O (10 mL, 556 mmol) with the mole ratio of 1:0.52:0.71:1324 was stirred briefly before heating to 120 °C for 72 h. After cooling to room temperature, the solvent was allowed to evaporate to near dryness. The initial and final pH values were 2 and 1, respectively. Light green **(10)** and dark green **(12)** blocks suitable for X-ray diffraction were isolated in 5% and 15% yield, respectively. IR (KBr pellet, cm⁻¹): **(10)** 3725(m), 3428(m), 3100(m), 2344(m), 1655(w), 1599(w), 1509(m), 1478(m), 1428(m), 1310(w), 1099(s), 1070(m), 1019(m), 936(s), 801(m), 711(w), 574(m), 507(w). Com-

pound **(12)** 3422 (m), 3087(w), 2906(w), 2379(w), 2278(w), 1476(m), 1424(s), 12614(m), 1235(m), 1216(m), 1159(m), 1109(m), 1053(m), 1021(s), 1003(s), 936(s), 785(s), 563(s). Anal. Calc. for $C_{28}H_{34}CuN_{3}O_{14}P$: C, 40.8; H, 4.13; N, 5.10. Found: C, 40.7; H, 4.06; N, 5.21%. Anal. Calc. for $C_{40}H_{40}CuN_{6}O_{14}O_{4}$: C, 44.5; H, 3.70; N, 7.78. Found: C, 43.9; H, 3.56; N, 7.66%.

2.12. Synthesis of $[Cu_2(tpypyz)(HO_3PC_8H_8PO_3H)_2] \cdot 2H_2O$ (**11** $\cdot 2H_2O$)

A solution of copper(II) acetate monohydrate (0.084 g, 0.421 mmol), tetra-2-pyridinylpyrazine (0.085 g, 0.22 mmol), o-xylene-diphosphonic acid (0.080 g, 0.30 mmol), and H₂O (10 mL, 556 mmol) with the mole ratio of 1:0.52:0.71:1321 was stirred briefly before heating to 120 °C for 72 h. The initial and final pH values were 4 and 4, respectively. Green rods suitable for X-ray diffraction were isolated in 80% yield. IR (KBr pellet, cm⁻¹): 3435(m), 3077(w), 2914(w), 2892(w), 2367(w), 2344(w), 1601(m), 1477(m), 1419(m), 1304(w), 1259(m), 1165(m), 1113(s), 1067(s), 1022(m), 903(s), 786(s), 711(m), 576(m), 526(m), 483(m). *Anal.* Calc. for C₇₂₋H₈₂Cl₆Cu₄N₁₂O₂₆P₆: C, 39.5; H, 4.04; N, 7.67. Found: C, 39.7; H, 3.86; N, 7.55%.

2.13. Synthesis of Cu(2,2' dipyidylamine)(HO₃PC₈H₈PO₃H) (13)

solution of copper(II) А acetate monohydrate (0.094 g,0.47 mmol), 2,2' dipyridylamine (0.074 g,0.432 mmol), *m*-xylene diphosphonic acid (0.152 g,0.57 mmol), (10 mL, 556 mmol) and HF (500 μ L, 14.5 mmol) with the mole ratio of 1:0.92:1.2:1183:30.8 was stirred briefly before heating to 135 °C for 48 h. The initial and final pH values were 1 and 1, respectively. Green rods suitable for X-ray diffraction were isolated in 90% yield. IR (KBr pellet, cm⁻¹): 3434(m), 2920(w), 2366(w), 2344(w), 1605(m), 1585(w), 1533(w), 1490(s), 1435(m), 1233(w), 1159(s), 1122(m), 1100(s), 948(m), 805(w), 765(m), 705(m), 530(w), 203(m), 465(w). Anal. Calc. for C36H38Cu2N6O12P4: C, 43.3; H, 3.84: N, 8.42. Found: C, 42.7; H, 3.76; N, 8.22%.

2.14. X-ray crystallography

Crystallographic data for all compounds were collected at low temperature (90 K) on a Bruker Kappa APEX II diffractometer equipped with an APEX II CCD system using Mo Ka radiation $(\lambda = 0.71073\text{\AA})$ [48,49]. The data were corrected for Lorentz and polarization effects [50], and adsorption corrections were made using sadabs [51]. The structures were solved by direct methods, and refinements were made using the SHELXTL [52] crystallographic software. After first locating all of the nonhydrogen atoms from the initial solution of each structure, the models were refined against F^2 using first isotropic and then anisotropic thermal displacement parameters until the final value of Δ/σ_{max} was less than 0.001. Hydrogen atoms were introduced in calculated positions and refined isotropically. Neutral atom scattering coefficients and anomalous dispersion corrections were taken from the International Tables, Vol. C. Crystallographic details for the structures of 1-13 are summarized in Table 1. Selected bond lengths and angles for the structures are given in Table 2. Images of the crystal structures were generated using CrystalMaker® [53].

2.15. Thermogravimetric analyses

TGA data were collected on a TA instruments Q500 v6.7 Thermogravimetric Analyzer. Data was collected on samples that ranged between 5 and 10 mg , ramping the temperature at 10 $^{\circ}$ C/min between ~25–800 $^{\circ}$ C.

Table 1

Summary of crystal data for the compounds of this study.

	$[Cu_2(H_2O)_2(O_3PC_8H_8PO_3)] (1)$	[Cu(H ₂ O)(o-phen)(HO ₃ PC ₈ H ₈ PO ₃ H)]·3H ₂ ((2 ·3H ₂ O)	D [Cu ₂ (H ₂ O) ₂ (o-phen) ₂ (O ₃ PC ₈ H ₈ PO ₃)]⋅6H ₂ O (3 ⋅6H ₂ O)
Empirical	CuPO ₄ C ₄ H ₆	$Cu_2P_4O_{20}N_4C_{40}H_{52}$	CuPO ₇ N ₂ C ₁₆ H ₂₀
Formula	212.60	1159.82	446.85
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	P1	P1
a (Å)	10.7962(19)	7.291(4)	6.8782(12)
b (Å)	7.5630(13)	11.546(6)	11.792(2)
c (Å)	7.3761(12)	13.795(7)	11.808(2)
α (°)	90.00	99.645(9)	116.021(3)
β (°)	92.646(3)	93.331(8)	93.494(3)
γ (°)	90.00	98.882(8)	95.651(3)
$V(Å^3)$	601.63(18)	1126.9(11)	850.6(3)
Ζ	4	1	2
D_{calc} (g cm ⁻³)	2.347	1.709	1.745
μ (mm $^{-1}$)	3.836	1.173	1.423
T (K)	90	90	90
Wavelength	0.71073	0.71073	0.71073
R_1^a	0.0233	0.0295	0.0534
wR ₂ ^b	0.0636	0.0806	0.1677
Empirical	[Cu(o-phen)(HO ₃ PC ₈ H ₈ PO ₃ H)]·3H ₂ O (4 ·3H ₂ O) CuP ₂ O ₉ N ₂ C ₂₀ H ₂₄	$\begin{array}{l} [Cu(\textit{o-phen})(HO_3PC_8H_8PO_3H)]~(\textbf{5}) \\ CuP_2O_6N_2C_{20}H_{18} \end{array}$	$\begin{array}{l} [Cu(\textit{o-phen})(HO_3PC_8H_8PO_3H)] \ (\textbf{6}) \\ CuP_2O_6N_2C_{20}H_{18} \end{array}$
Formula weight	561.89	507.84	507.84
Crystal system	triclinic Pī	monoclinic P2 ₃ /n	triclinic Pī
a (Å)	10.6221(8)	10 3496(18)	97161(16)
h(Å)	10,9369(9)	14 682(3)	11 3506(18)
c(Å)	11 4714(9)	12 523(2)	11 3710(18)
α (°)	66 8400(10)	90.00	116 331(2)
β(°)	64.8830(10)	104.644(4)	111.017(3)
ν (°)	84.0880(10)	90.00	92.971(3)
$V(Å^3)$	1106.13(15)	1841.1(5)	1015.3(3)
Z	2	4	2
D_{calc} (g cm ⁻³)	1.687	1.832	1.661
μ (mm ⁻¹)	1.189	1.407	1.276
T (K)	90	90	90
Wavelength	0.71073	0.71073	0.71073
R_1^a	0.0279	0.0284	0.0200
wR ₂ ^b	0.0733	0.0663	0.0576
	[Cu ₂ (H ₂ O) ₂ (bpy) ₂ (HO ₃ PC ₈ H ₈ PO ₃ H ₂) ₂ (HO ₃ PC ₈ H ₈ PO ₃ H)]·2H ₂ O (7 ·2H ₂ O)	[Cu(bpy)(HO ₃ PC ₈ H ₈ PO ₃ H)]·2H ₂ O (8 ·2H ₂ C	$O) [Cu(bpy)(HO_3PC_8H_8PO_3H)] (9)$
Empirical formula	$CuP_{3}O_{11}N_{2}C_{22}H_{28}$	$CuP_2O_8N_2C_{18}H_{22}$	$CuP_2O_6N_2C_{18}H_{18}$
Formula weight	652.91	519.86	483.82
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	P1	P1
a (A)	9.8285(17)	9.9436(13)	9.7629(14)
b (A)	16.843(3)	10.0660(14)	10.7730(16)
<i>c</i> (A)	16.124(3)	11.3028(15)	11.3060(17)
α (°)	90.00	110.062(2)	62.814(2)
β(°)	106.353(2)	108.237(2)	89.181(3)
γ(*) V (Å3)	90.00	91.260(2)	076 = (2)
V (A')	2301.1(8)	998.0(Z)	970.3(2) 2
$D = (\pi \mathrm{cm}^{-3})$	4	2 1 729	2 1.646
$\mu (\text{mm}^{-1})$	1 105	1 306	1 322
$T(\mathbf{K})$	90	90	90
Wavelength	0.71073	0.71073	0.71073
R_1^a	0.0280	0.0490	0.0267
wR ₂ ^b	0.0854	0.1108	0.0709
Empirical formu Formula weight Crystal system Space group	$ [Cu_2(H_2O)_2(tpypyz)(HO_3PC_8H_8PO_3H)_2] \cdot (H_2O_3PC_8H_8PO_3H)_2] \cdot (H_2O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O) \\ [10] (H_2O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O) \\ [10] CuP_4O_14N_3C_{28}H_{34} \\ 824.00 \\ triclinic \\ P\bar{1} \\ 10.7212(10) \\] \\ \end{tabular}$	2)2·2H2O [() 1 t t	Cu ₂ (tpypyz)(HO ₃ PC ₈ H ₈ PO ₃ H) ₂]·2H ₂ O 11·2H ₂ O) Cu ₂ P ₄ O ₁₄ N ₆ C ₄₀ H ₄₀ 079.74 riclinic $v_1^{\overline{1}}$
a(A)	IU./3I3(Ib) 11.4004(16)	8	0.759(b) 0.008(6)
D (A)	11.4004(10)		

	14.482(2) 78.920(2) 78.942(2) 75.774(2) 1665.8(4) 2 1.643 0.922 90 0.71073 0.71073 0.0294 0.0816	13.506(9) 89.597(11) 86.049(10) 71.486(9) 1008.0(12) 1 1.779 1.295 90 0.71073 0.0259 0.0757
Empirical formula Formula weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z D_{calc} (g cm ⁻³) μ (mm ⁻¹) T (K) Wavelength R_1^a wn b	[Cu ₄ Cl ₄ (tpypyz) ₂ (H ₂ O ₃ PC ₈ H ₈ PO ₃ H) ₂]Cl ₂ ·H ₂ O ₃ PC ₈ H ₈ PO ₃ H ₂ ·8H ₂ O (12 ·H ₂ O ₃ PC ₈ H ₈ PO ₃ H ₂ ·8H ₂ O) Cu ₄ Cl ₆ P ₆ O ₂₆ N ₁₂ C ₇₂ H ₈₂ 2184.18 monoclinic C2/c 14.0898(15) 20.701(3) 29.256(4) 90.00 8526.9(17) 4 1.694 1.370 90 0.71073 0.0551 0.128	$ \begin{bmatrix} Cu(2,2'dipyidylamine)(HO_3PC_8H_8PO_3H) \end{bmatrix} (13) \\ Cu_2P_4O_{12}N_6C_{36}H_{38} \\ 997.68 \\ triclinic \\ P\bar{1} \\ 9.722(4) \\ 10.629(4) \\ 10.723(4) \\ 68.927(6) \\ 67.969(6) \\ 75.033(6) \\ 948.6(6) \\ 1 \\ 1.746 \\ 1.365 \\ 90 \\ 0.71073 \\ 0.0282 \\ 0.0700 \\ \end{bmatrix} $

^a $R_1 = \Sigma |F_0| - |F_c| / \Sigma |F_0|.$ ^b $wR_2 = \{ \Sigma [w(F_0^2 - F_c^2)^2] \sum [w(F_0^2)^2] \}^{1/2} \}.$

2.16. Magnetic susceptibility studies

Magnetic measurements were performed on a Quantum Design SQUID, MPMS-XL magnetometer. Magnetic susceptibility measurements for the complexes of this study were carried out in the direct current (dc) mode in an applied field of 0.1 T in the 2-300 K range. The measurements were performed on polycrystalline samples of compound at 1000 Oe. Magnetic data obtained for samples were corrected for diamagnetic contributions by the use of the Pascal constants.

3. Results and discussion

3.1. Syntheses

Hydrothermal methods were first applied for the synthesis of zeolites and metal phosphates [54,55]. More recently, the technique has been extended to the routine synthesis of metal oxides and organic-inorganic composite materials [56-59]. Hydrothermal syntheses are conventionally carried out in water at 120-250 °C at autogenous pressure. Product composition depends on a number of critical conditions, including pH of the medium, temperature and hence pressure, the presence of structure-directing cations, and the use of mineralizers. Since a variety of cationic and anionic components may be present in solution, those of appropriate size, geometry and charge to fulfill crystal packing requirements may be selected from the mixture in the crystallization process. The technique thus exploits "self-assembly" of a solid phase from soluble precursors at moderate temperatures.

Hydrothermal methods have been exploited for decades in the preparation of metal-diphosphonate materials with pillared layer structures, such as that of the parent compound $[Cu_2(H_2O)_2(1,4-O_3-$ PC₈H₈PO₃)] (1). The introduction of auxiliary ligands, such as ophenanthroline and 2,2'-bipyridyl, provides a method for reducing the overall dimensionality of the phase by blocking coordination sites at the metal and preventing structural expansion in one or more dimensions. The chain structures of compounds 3, 6 and 9 and the layers associated with compounds 4, 5 and 8 are characteristic examples of the use of simple auxiliary chelates in the design of lower dimensional materials.

However, such naïve design principles did not extend to the chemistry of the Cu(II)/tpyprz/xylyl-diphosphonate system. Our expectation was that the dipodal tpyprz would bridge copper sites of copper-diphosphonate chains or networks to provide two- or three-dimensional materials, or would decorate the surfaces of chains or networks. Rather unexpectedly, only compound 10 exhibited a chain structure while molecular species were observed for 11 and 12: a binuclear compound and a tetranuclear material, respectively. In fact, the notable feature of the structural chemistry of the copper(II)/xylyl-diphosphonate/organoimine chelate system is the unusually high incidence of molecular species: in addition to 11 and 12, compounds 2, 7 and 13 are also molecular. This observation also correlates with the tendency of the xylyl-diphosphonate ligands to adopt a variety of protonated forms, rather than the more common fully deprotonated tetranegative anion $\{O_3P-R-PO_3\}^{4-}$. As noted previously [26], changes in the organic tether of the diphosphonate ligand result in profound structural consequences. In comparing the xylyl-diphosphonates and the phenyl-diphosphonates, the behavior may reflect simply the different pK values of the parent acids, as well as the geometric consequences of the increased flexibility of the xylyl tether compared to the phenyl spacer.

The infrared spectra of compounds 1-13 exhibit a pattern of two or three medium to strong bands in the $1000-1200 \text{ cm}^{-1}$ range attributed to v(P-O) of the phosphonate ligands. In addition, compounds 2-4, 7-8, and 10-12 exhibit an intense broad band at ca. 3100 cm^{-1} assigned to v (O–H) of the coordinated water molecules.

3.2. Description of the X-ray structures of 1-13

The parent material, $[Cu_2(H_2O)_2(1,4-O_3PCH_2C_6H_4CH_2PO_3)]$ (1), exhibits the prototypical pillared layer structure common to a host

Table 2		
Selected bond lengths (Å) and	angles (°) for the compounds	of this study.

$[Cu_2(H_2O)_2(O_3PC_8H_8PO_3)]$ (1)	1017(2)	02 6-1 04	102.02(8)
Cu1 03	1.917(2)	03 Cu1 04 02 Cu1 01	163.02(8)
Cu1 02	1.975(2)	03 Cu1 04	107.63(7)
Cu1 01	2.010(2)		
Cu1 04	2.351(2)		
P1 02	1.534(2)		
PI 03 P1 04	1.536(2)		
$[G_{1}(U, Q)]$ (a phan)(UQ, DC, U, DQ, U)] (2U, Q, (2, 2U, Q))	1.5 10(2)		
$C_{11} \cap C_{2} \cap C_{11} \cap C_{2} \cap C_{$	1 930(2)	04 Cu1 N1	17080(7)
Cu1 02	1.935(2)	02 Cu1 N2	165.99(7)
Cu1 N1	2.004(2)		
Cu1 N2	2.014(2)		
	2.233(2)		
P1 02	1.507(2) 1.512(2)		
P1 O3(H)	1.571(2)		
P2 07	1.497(2)		
P2 05	1.502(2)		
P2 O6(H)	1.587(2)		
$[Cu_2(H_2O)_2(o-phen)_2(O_3PC_8H_8PO_3)] \cdot 6H_2O$ (3 ·6H ₂ O)			
Cu1 01	1.924(2)	01 Cu1 N2	165.75(17)
Cu1 03	1.931(2) 2.026(2)	03 Cu1 N1 03 Cu1 02	100.90(17) 102.68(16)
Cu1 N2	2.038(2)	05 Cur 02	102.00(10)
Cu1 02	2.265(2)		
P1 04	1.502(2)		
P1 01	1.528(2)		
P1 03	1.538(2)		
$[Cu(o-phen)(HO_3PC_8H_8PO_3H)]\cdot 3H_2O (4\cdot 3H_2O)$	1.0.42(2)	00.0.4 NO	100 15(7)
	1.943(2)	03 Cu1 N2	168.15(7)
Cu1 N2	2.011(2)	OT CUT NI	105.02(7)
Cu1 N1	2.030(2)		
Cu1 02	2.220(2)		
P1 03	1.512(2)		
P1 01	1.513(2)		
P1 04(H) P2 02	1.509(2) 1.507(2)		
P2 06	1.513(2)		
P2 O5(H)	1.582(2)		
$[Cu(o-phen)(HO_3PC_8H_8PO_3H)]$ (5)			
Cu1 O4	1.943(2)	04 Cu1 N1	157.54(8)
Cu1 02	1.989(2)	02 Cu1 N2	158.68(7)
Cu1 N1	2.045(2)	02 Cu1 01	100.29(7)
	2.030(2) 2.154(2)	N1 Cu1 O1	102.89(7) 100.57(7)
P1 04	1.508(2)		100.57(7)
P1 O2	1.529(2)		
P1 O3(H)	1.566(2)		
P2 01	1.502(2)		
P2 05 P2 06(H)	1.512(2) 1 599(2)		
$\left[C_{\rm e}(a, a, b, a, b)\right] (10, \rm DC, 11, \rm DO, 11) \left[(C_{\rm e})\right]$	1.555(2)		
$[Cu(0-piten)(HO_3PC_8H_8PO_3H)](0)$ Cu1 O2	1 912(2)	02 Cu1 N2	170 28(5)
Cu1 01	1.948(2)	01 Cu1 N1	148.31(5)
Cu1 N2	2.011(2)	01 Cu1 03	111.94(5)
Cu1 N1	2.028(2)		
Cu1 03	2.238(2)		
PI 02 P1 03	1.513(2)		
P1 O4(H)	1.570(2)		
P2 05	1.505(2)		
P2 01	1.511(2)		
P2 O6(H)	1.580(2)		
$[Cu_2(H_2O)_2(bpy)_2(HO_3PC_8H_8PO_3H_2)_2]$			
$(HO_3PC_8H_8PO_3H)]\cdot 2H_2O(7\cdot 2H_2O)$	1.060/2)	02 Cu1 N1	167.02(0)
Cui 05 Cui N1	1.909(2) 2.007(2)	US CUI NI	ισ <i>ι</i> .02(6)
Cu1 N2	2.015(2)		
Cu1 01	2.217(2)		
P1 02	1.494(2)		

P1 06 P1 07(H) P2 03 P2 05 P2 04 P3 08 P3 010 [*] P3 09 [*]	$\begin{array}{c} 1.528(2)\\ 1.562(2)\\ 1.523(2)\\ 1.533(2)\\ 1.534(2)\\ 1.480(2)\\ 1.528(2)\\ 1.717(2) \end{array}$		
[<i>Cu</i> (<i>bpy</i>)(<i>HO</i> ₃ <i>PC</i> ₈ <i>H</i> ₈ <i>PO</i> ₃ <i>H</i>)]-2 <i>H</i> ₂ <i>O</i> (8 -2 <i>H</i> ₂ <i>O</i>) <i>Cu</i> 1 O2 <i>Cu</i> 1 O1 <i>Cu</i> 1 N1 <i>Cu</i> 1 N2 <i>Cu</i> 1 O3 P1 O3 P1 O6 P1 O5 P2 O1 P2 O2 P2 O4(H)	$\begin{array}{c} 1.946(2)\\ 1.965(2)\\ 2.000(2)\\ 2.006(2)\\ 2.266(2)\\ 1.517(2)\\ 1.537(2)\\ 1.545(2)\\ 1.516(2)\\ 1.516(2)\\ 1.566(2) \end{array}$	O2 Cu1 N1 O1 Cu1 N2 N1 Cu1 O3	164.04(15) 166.11(15) 101.93(14)
[Cu(bpy)(HO ₃ PC ₈ H ₈ PO ₃ H)] (9) Cu1 O2 Cu1 O3 Cu1 N2 Cu1 N1 Cu1 O1 P1 O2 P1 O1 P1 O6(H) P2 O4 P2 O3 P2 O5(H)	$\begin{array}{c} 1.916(2)\\ 1.947(2)\\ 2.003(2)\\ 2.017(2)\\ 2.294(2)\\ 1.517(2)\\ 1.522(2)\\ 1.570(2)\\ 1.570(2)\\ 1.506(2)\\ 1.515(2)\\ 1.580(2) \end{array}$	O2 Cu1 N2 O3 Cu1 N1 O3 Cu1 O1	171.78(5) 150.33(6) 111.67(5)
$ \begin{bmatrix} Cu_2(H_2O)_2(tpypyz)(H_2O_3PC_8H_8PO_3H)_2 (HO_3PC_8H_8PO_3H)] \\ \cdot (H_2O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O (10 \cdot (H_2O_3PC_8H_8PO_3H_2)_2 \cdot 2H_2O) \end{bmatrix} \\ Cu1 03 \\ Cu1 03 \\ Cu1 02 \\ Cu1 N2 \\ Cu1 N3 \\ Cu1 N1 \\ Cu1 01 \\ P1 02 \\ P1 06 \\ P1 07(H) \\ P2 09 \\ P2 08 \\ P2 010(H) \\ P3 03 \\ P3 05 \\ P3 04(H) \\ P4 011 \\ P4 012 \\ P4 013(H) \end{bmatrix} $	$\begin{array}{c} 2.588(2)\\ 1.904(2)\\ 1.957(2)\\ 2.026(2)\\ 2.049(2)\\ 2.244(2)\\ 1.518(2)\\ 1.563(2)\\ 1.563(2)\\ 1.563(2)\\ 1.564(2)\\ 1.564(2)\\ 1.514(2)\\ 1.514(2)\\ 1.573(2)\\ 1.480(2)\\ 1.555(2)\\ 1.561(2)\end{array}$	O2 Cu1 N2 O2 Cu1 N1 N3 Cu1 N1	172.87(7) 101.70(7) 159.12(7)
[Cu ₂ (tpypyz)(HO ₃ PC ₈ H ₈ PO ₃ H) ₂]-2H ₂ O (11 -2H ₂ O) Cu1 01 Cu1 N2 Cu1 N3 Cu1 N1 Cu1 O2 P1 01 P1 06 P1 05 P2 02 P2 03 P2 04	$\begin{array}{c} 1.892(2)\\ 1.971(2)\\ 2.009(2)\\ 2.024(2)\\ 2.112(2)\\ 1.508(2)\\ 1.525(2)\\ 1.528(2)\\ 1.493(2)\\ 1.533(2)\\ 1.533(2)\\ 1.535(2) \end{array}$	01 Cu1 N2 01 Cu1 N1 N3 Cu1 N1 01 Cu1 02	164.12(6) 101.87(8) 152.67(7) 105.10(7)
[Cu ₄ Cl ₄ (tpypyz) ₂ (H ₂ O ₃ PC ₈ H ₈ PO ₃ H) ₂]Cl ₂ ·H ₂ O ₃ PC ₈ H ₈ PO ₃ H ₂ ·8H ₂ O (12 ·H ₂ O ₃ PC ₈ H ₈ PO ₃ H ₂ ·8H ₂ O) Cu1 N2 Cu1 N3 Cu1 N1 Cu1 N1 Cu1 Cl1 Cu1 O2 Cu2 N5 Cu2 N4 Cu2 N6 Cu2 Cl2 Cu2 Cl2 Cu2 O1	1.971(2) 2.021(2) 2.025(2) 2.216(2) 2.263(2) 1.948(2) 2.013(2) 2.021(2) 2.199(2) 2.324(2)	N3 Cu1 N1 N2 Cu1 Cl1 Cl1 Cu1 O2 N4 Cu2 N6 N5 Cu2 Cl2 N6 Cu2 Cl2 Cl2 Cu2 O1	$\begin{array}{c} 157.78(16)\\ 166.28(12)\\ 103.59(9)\\ 159.34(17)\\ 164.85(13)\\ 100.61(12)\\ 106.35(9) \end{array}$

(continued on next page)

P1 02 P1 03 P1 01(H) P2 04 [*] P2 06 [°] P2 05 P3 09	1.522(2) 1.530(2) 1.563(2) 1.535(2) 1.522(2) 1.559(2) 1.503(2)		
P3 08	1.529(2)		
P3 07(H)	1.568(2)		
[Cu(2,2'dipyidylamine)(HO ₃ PC ₈ H ₈ PO ₃ H)] (13)			
Cu1 02	1.911(2)	O1 Cu1 N3	153.60(8)
Cu1 01	1.922(2)	O2 Cu1 N1	150.28(8)
Cu1 N3	1.966(2)		
Cu1 N1	1.977(2)		
P1 O2	1.514(2)		
P1 O1	1.518(2)		
P1 O3(H)	1.567(2)		
P2 04	1.490(2)		
P2 06	1.529(2)		
P2 O5(H)	1 582(2)		

* Indicates disordered oxygen atom.

metal-diphosphonate phases and specifically to copper(II)-diphosphonate materials (Fig. 1a). The structure of the inorganic layer $\{Cu_2(H_2O)_2(O_3P-)\}_n$ is similar to that previously observed for $[Cu_2(H_2O)_2(1,4-O_3PC_6H_4PO_3)]$ [17]. The building block is a binuclear unit of edge-sharing copper(II) square pyramids, linked to adjacent binuclear units through bridging $\{O_3P-\}$ groups. The coordination geometry at each copper site is defined by three phosphonate oxygen donors and an aqua ligand in the basal plane, with a fourth phosphonate oxygen occupying the apical position. Thus, each cop-

per square pyramid shares a corner with four phosphorus tetrahedra and each phosphorus tetrahedron shares corners with four copper square pyramids.

The connectivity pattern generates three distinct heterocyclic units within the inorganic network. The first is the $\{Cu_2O_2\}$ ring associated with the edge-sharing interaction of copper square pyramids. The remaining rings are the common $\{M_2(2-O_3PR)_2\}$ building units observed in many metal-organophosphonate structures. One of these adopts the chain configuration of Fig. 1c or the DIV



Fig. 1. (a) A mixed polyhedral and ball-and-stick representation of the pillared-layer structure of $[Cu_2(H_2O)_2(1,4-O_3PC_8H_8PO_3)](1)$; (b) a view of the structure of the inorganic layer of **1**. Color scheme: copper, blue polyhedra or spheres; phosphorus, yellow tetrahedra or spheres; oxygen, red spheres; carbon, black spheres. This scheme is used throughout. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. A view of the molecular structure of $[Cu(H_2O)(o-phen)(1,4-HO_3PC_8H_8PO_3H)]$ (2). Color scheme: as above; nitrogen, light blue spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

di-phosphato (O,O') bridge mode of the scheme proposed by Beltran-Porter et al. [60]. The second adopts a bowl-like configuration due to edge-sharing to an adjacent copper site at one copper terminus. This latter ring is akin to the DIII bridging mode of the Beltran-Porter classification.

When o-phenanthroline is introduced as a coligand, the molecular 1-D and 2-D structures of $[Cu(H_2O)(o-phen)(1,4-HO_3PCH_2C_6H_4CH_2PO_3H)]\cdot 3H_2O$ (2·3H₂O), $[Cu_2(H_2O)_2(O_3PCH_2C_6H_4CH_2PO_3)]\cdot 3H_2O$ (3-3H₂O) and $[Cu(o-phen)(HO_3PCH_2C_6H_4CH_2PO_3H)]\cdot 3H_2O$ (4·3H₂O), respectively, are observed.

As shown in Fig. 2, the molecular structure of **2** consists of binuclear copper(II) units. The copper geometry is '4+1' axially elongated square pyramidal, with the nitrogen donors of the *o*-phen ligand and oxygen donors from two diphosphonate ligands in the basal plane and an aqua ligand defining the apical position. The structure exhibits the common $\{Cu_2(_2-O,O'phosphonate)_2\}$ core. Only one terminus of each diphosphonate ligand is coordinated, while the other is pedant and protonated. One oxygen site at either terminus of the diphosphonate ligand is protonated, as indicated by the P–O bond distances of 1.571(2)Å and 1.588(2)Å for P1–O3(H) and P2–O6(H), respectively, compared to an average length of 1.505(3)Å for all other P–O bonds of the structure.

The one-dimensional structure of **3**, shown in Fig. 3, is constructed from the common $\{Cu_2(_2-O,O'-phosphonate)_2\}$ units linked through the organic tether of the diphosphonate ligand. The copper sites once again display square pyramidal geometry with the basal plane occupied by the *o*-phen nitrogen donors and two phosphonate oxygen donors and a water molecule in the apical position. The aqua ligands assume an *anti*-orientation with respect to the $\{-Cu-O-P-O-\}_2$ ring. The structural influence of the *o*-phen ligand is apparent in this instance. By occupying two coordination sites on the copper, the ligand prevents expansion into the pillared layered prototype for metal-diphosphonate structures. However, the aqua ligand occupying the apical coordination site is available for substitution and, consequently, for structural expansion into two-dimensions as illustrated by compound **4**, shown in Fig. 4.

The network structure of **4** is constructed from the recurring building units $\{Cu_2(_2-O,O'-phosphonate)_2\}$ linked through diphosphonate ligands into a layer structure. The structure may be described as $\{Cu_2(HO_3PCH_2C_6H_4CH_2PO_3H)_2\}$ chains, nearly identical to those of compound **3** and running parallel to the crystallographic *c*-axis, connected through the diphosphonate ligands. Thus, each binuclear subunit is linked to two adjacent subunits in the chain and to two adjacent chains through the dipodal ligands.

The o-phen coligands project above and below the layer and serve to prevent structural expansion in the third dimension. The chain substructure of **4** is clearly derived from that of **3** with displacement of the aqua ligands by additional diphosphonate linkers providing the expansion into two-dimensions. This observation suggests that the chain of **3** may be a precursor to the formation of the two-dimensional structure of **4** and consequently represents a kinetic product.

It is noteworthy that either terminus of the diphosphonate ligand is protonated. The protonation sites are clearly established by the P–O bond distances of 1.569(2) Å and 1.583(2) Å for the protonated P1–O4(H) and P2–O5(H) sites and of 1.512(3) Å for the average of all others.

The structural consequences of modifying the relative positions of the $\{O_3P_-\}$ units on the ring are illustrated by the structures of $[Cu(o-phen)(1,2-HO_3PCH_2C_6H_4CH_2PO_3H)]$ **(5**) and [Cu(o phen)(1,3-HO₃PCH₂C₆H₄CH₂PO₃H)] (6). As shown in Fig. 5, the general connectivity pattern for 5 is similar to that observed for 4. Thus, the common $\{Cu_2(2-0,0'-phosphonate)_2\}$ core connected through doubly protonated {HO₃PC₈H₈PO₃H}²⁻ ligands provides the recurring structural motif. Once again each phosphonate ligand bridges two adjacent binuclear cores and each binuclear unit is in turn linked to four adjacent units. The major structural consequence of shifting the relative positions of the $\{O_3P_-\}$ groups from 1,4 in **4** to 1,2 in **5** is the relative packing of polyhedra within the layer, as shown in Fig. 5c.

While the structure of 1,3-xylenediphosphonate derivative **6** is one-dimensional, it is quite distinct from the 1-D structure of **3**. As shown in Fig. 6, the structure consists of the common $\{Cu_2(_2-O,O'-phosphonate)_2\}$ secondary building units linked through the tethers of dipodal ligands. In contrast to **3**, the aqua ligand has been displaced by an oxygen donor of a $\{1,3-HO_3PC_8H_8PO_3H\}^{2-}$ ligand. As a result each binuclear copper subunit is linked to two adjacent units of the chain through four diphosphonate linkers, rather than



Fig. 3. A ball-and-stick representation of the one-dimensional structure of [Cu₂(H₂O)₂(1,4-O₃PC₈H₈PO₃)] (3).



Fig. 4. (a) Ball-and-stick view of the layer structure of [Cu(*o*-phen)(1,4-HO₃PC₈H₈PO₃H)] (**4**) viewed approximately in the *ac* plane; (b) a polyhedral representation of the structure viewed edge-onto the plane, parallel to the *o*-axis.



Fig. 5. Polyhedral and ball-and-stick representation of the two-dimensional structure of [Cu(*o*-phen)(1,2-HO₃PC₈H₈PO₃H)] (**5**) in the *bc* plane.



Fig. 6. A view of the one-dimensional structure of $[Cu(o-phen)(1,3-HO_3PC_8H_8PO_{3-}H)]$ (6).

two as in the structure of **3**. The diphosphonate ligands again adopt the $\{HO_3PC_8H_8PO_3H\}^{2-}$ protonation mode with O4 and O6 as the clear protonation sites (P–OH distances of 1.570(1)Å and 1.580(1)Å compared to an average of 1.512(1)Å for all other P–O distances).

Substitution of o-phenanthroline by 2,2'-bipyridine provides the molecular $[Cu_2(H_2O)_2(bpy)_2(HO_3PCH_2C_6H_4CH_2PO_3H_2)(HO_3PCH_2C_6H_4PO_3H)]\cdot H_2O$ (7·H₂O), the two-dimensional $[Cu(bpy)(HO_3-PCH_2C_6H_4CH_2PO_3H)]\cdot 2H_2O$ (8·2H₂O) and the one-dimensional $[Cu(bpy)(HO_3PCH_2C_6H_4CH_2PO_3H)]$ (9).

The molecular structure of **7** consists of an unusual binuclear arrangement featuring copper(II) sites bridged through the $\{O_3P-\}$ termini of a single diphosphonate ligand (Fig. 7). The copper sites exhibit axially elongated square pyramidal geometry. The basal



Fig. 7. A view of the molecular structure of $[Cu_2(H_2O)_2(bpy)_2(1,4-HO_3PC_8H_8PO_3H_2)_2(1,4-HO_3PC_8H_8PO_3H)]$ (7).



Fig. 8. A view of the two-dimensional structure of $[Cu(bpy)(1,4-HO_3PC_8H_8PO_3H)]$ (8).

plane is defined by the nitrogen donors of the bpy ligand and oxygen donors from two diphosphonate ligands; an aqua ligand occupies the apical position. One diphosphonate ligand bonds to a single copper site through one oxygen donor, adopting the $\{HO_3.PC_8H_8PO_3H_2\}^{1-}$ protonation mode with one terminus pendant and doubly protonated. The second diphosphonate ligand bridges the two copper sites with oxygen atoms from either terminus. The molecular structure of **7** may be contrasted with that of **2** which adopts the more conventional $\{Cu_2(2-O,O'-phosphonate)_2\}$ core structure.

On the other hand, the two-dimensional structure of **8**, shown in Fig. 8, is analogous to that of **4**. The network consists of $\{Cu_2 (bpy)_2(HO_3PC_8H_8PO_3H)_2\}$ chains connected through the organic tethers of ligands to adjacent chains, in a fashion identical to that of **4**.

The one-dimensional structure of **9** is analogous to that of **6**, with the *o*-phen ligand replaced by bpy (Fig. 9). The conservation of certain structural motifs throughout the series of copper(II)/ diphosphonate/organonitrogen coligand series is not unexpected.

The introduction of the binucleating coligand tetrapyridinylpyrazine (tpyprz) unexpectedly results in a series of chain and molecular species, $[Cu_2(H_2O)_2tpyprz)(1,4-HO_3PCH_2C_6H_4CH_2PO_3H)_2]\cdot(H_2O_3PC_8H_8PO_3H_2)\cdot2H_2O$ ($10\cdot H_2O_3PC_8H_8PO_3H_2\cdot2H_2O$), $[Cu_2$ (tpyprz)(1,2-HO_3PCH_2C_6H_4CH_2PO_3H)_2]\cdot2H_2O ($11\cdot 2H_2O$) and $[CuCl_4$ (tpyprz)(1,4-H_2O_3PCH_2C_6H_4CH_2PO_3H)_2]Cl_2\cdot H_2O_3PC_8H_8PO_3H_2\cdot8H_2O ($12\cdot H_2O_3PC_8H_8PO_3H_2\cdot8H_2O$).

As shown in Fig. 10, the structure of **10** consists of $\{Cu_2(H_2O)_2 (tpyprz)(1,4-HO_3PCH_2C_2C_6H_4CH_2PO_3H)_2\}_n$ chains and H_2O and $H_2O_3PC_8H_8PO_3H_2$ molecules. The copper sites of the chains exhibit '4+2' axially distorted octahedral geometry with the pyridyl and pyrazine nitrogen donors of one end of the tpyprz ligand and a diphosphonate ligand in the equatorial plane and an aqua ligand and a phosphonate ligand coordinates to a copper site through a single oxygen donor of one –PO₃H terminus, leaving the second terminus pendant. The second organophosphonate ligand bridges copper centers from two adjacent $\{Cu_2(tpyprz)\}^{4+}$ binuclear units through one oxygen donor of either terminus. Expansion into one-dimension is thus achieved through this dipodal bridging ligand.

As shown in Fig. 10b, each uncoordinated phosphonic acid, H_2 -O₃PC₈H₈PO₃H₂ engages in hydrogen bonding to four adjacent chains to produce a hydrogen-bonded three-dimensional framework.

The molecular structure of **11** exhibits two square pyramidal copper(II) sites bridged by the tpyprz ligand (Fig. 11). The basal planes of the square pyramidal copper centers again display three nitrogen donors and a phosphonate oxygen in the basal plane. In contrast to **10**, the apical site is occupied by a second oxygen donor from a chelating 1,2-xylyldiphosphonate ligand. The incorporation of 1,2-xylyldiphosphonate derivative allows the chelate geometry which would be precluded with the 1,3- and 1,4- forms for steric and geometric reasons.



Fig. 9. The one-dimensional structure of [Cu(bpy)(1,3-HO₃PC₈H₈PO₃H)] (9).



Fig. 10. (a) A view of the one dimensional structure of $[Cu_2(H_2O)_2(tpyprz)(1,4-HO_3PC_8H_8PO_3H)_2]$ (**10**) and the associated $(1,4-H_2O_3PC_8H_8PO_3H_2)$ molecules of crystallization; (b) *a* view down the *a*-axis of four adjacent $[Cu_2(H_2O)_2(tpyprz)(1,4-HO_3PC_8H_8PO_3H)_2]$ chains and of the hydrogen bonding interactions with the interchain $(1,4-H_2O_3PC_8H_8PO_3H_2)$ molecule.

As illustrated in Fig. 12, the structure of **12** is tetranuclear and incorporates a chloride donor at each copper site. The copper sites are once again square pyramidal with three tpyprz nitrogen donors



Fig. 11. A view of the binuclear structure of $[Cu_2(tpyprz)(1,2\text{-}HO_3PC_8H_8PO_3H)_2]$ (11).

and a chloride in the basal plane and an apical phosphonate oxygen. The two $\{Cu_2(tpyprz)Cl_2\}^{2+}$ units of the tetramer are linked through two $\{H_2O_3PC_8H_8PO_3H\}^{1-}$ phosphonates, each of which connects copper sites from two binuclear units through oxygen donors of the $\{HO_3P-\}$ terminus while the other terminus is pendant and doubly protonated.

The introduction of 2,2'-dipyridylamine as the coligand provided a single material [Cu(dpa)(1,3-HO₃PCH₂C₆H₄CH₂PO₃H)] (**13**), whose structure is shown in Fig. 13. The molecular structure is similar to that of **2** with the exception that the apical aqua ligand of **2** has been lost in **11**. Consequently, the copper sites enjoy distorted square planar geometry. The ligand imposed steric requirements are apparent in the more relaxed N–Cu–N angle in **11** of 92.4(1)° compared to a bite angle of 81.7(1)° in **2**. The availability of the apical site as well as the presence of the pendant {O₃P–} groups suggest that compounds such as **13**, as well as **2**, **7**, **10** and **12** may serve as useful precursors for the syntheses of higher dimensionality or bimetallic phases.

3.3. Thermal analyses

The thermal gravimetric analysis (TGA) plots of the compounds of this study are quite complicated as there is a range of starting Cu:P ratios, some of which do not match the stable phosphate phases expected as the final decomposition products. Also, the



Fig. 12. The structure of the molecular, tetranuclear $[Cu_4Cl_4(tpyprz)_2(1,4-H_2O_3PC_8-H_8PO_3H)_2]^2$ anion. Color scheme: as above with chlorine as light green spheres.

decomposition processes do not appear to be complete even at 800 °C, as evidenced by a gradual loss continuing at the limiting temperature of our instrument. All TGA profiles can be found in the ESI..

The TGA of compound **1** shows an initial weight loss of ca. 8.0% corresponding to the loss of the weakly coordinated water ligands (8.5%, theoretical). This initial weight loss is followed by a series of overlapping weight losses starting at 250 °C and continuing to 800 °C. Over this range there are three processes occurring: the condensation of the hydrogen phosphonate groups, the pyrolysis of the organic group, and the oxidation and loss of P_2O_5 [63]. This decomposition pattern likely results in a mixture of final products. Powder XRD analysis of the pyrolysis product shows that it contains $Cu_2P_2O_7$. However, the observed loss of ca. 34.5% suggests further decomposition to a mixture of $Cu_2P_2O_7$ and CuO.

The TGA of compound **2** exhibits a generally similar pattern with an initial weight loss between room temperature and 125 °C attributed to the loss of water of crystallization. This dehydration process is followed by a plateau of stability between 125 °C and 250 °C. Subsequently, a pattern of overlapping weight losses between 250 °C and 500 °C may correspond to the condensation of the hydrogen phosphonate groups, the pyrolysis of the phosphonate organic group, and the oxidation and loss of P₂O₅, as observed for compound **1**. The loss of the coordinated water molecules also



Fig. 13. The molecular structure of [Cu(2,2-dpy)(HO₃PC₈H₈PO₃H)] (13).



Fig. 14. The dependence of the magnetic susceptibility χ (•) and effective magnetic moment μ_{eff} (\bigcirc) of [Cu(*o*-phen)(1,4-HO₃PC₈H₈PO₃H)] (**4**) on temperature *T*. The line drawn through the data is the fit to the Curie–Weiss law.

occurs in this range. The mechanism of dehydration is dependent on topological and energetic considerations [64] such that it is expected that accessibility of water molecules to existing void spaces in the crystal would result in low liberation temperatures as noted for the waters of crystallization. On the other hand, the evacuation of coordinated water requires higher temperature as these are constrained by the metal coordination sphere and do not have facile access to the void spaces. The weight loss continuing beyond 800 °C is attributed to the pyrolysis of the *o*-phen ligand and the production of the final products, most likely a mixture of $Cu_2P_2O_7$ and CuO.

Similar profiles are observed for compounds **3**, **4**, **7**, **8**, **10**, **11** and **12** which contain water molecules of crystallization. The profiles for compounds **5**, **6**, **9** and **13** are similar in the region above 250 °C but show no weight loss below that temperature since there is no water of crystallization associated with these compounds.

3.4. Magnetism

Magnetic susceptibility measurements of complexes **1**, **2**, **4–8**, and **11–13** were performed on polycrystalline samples of compound at 1000 Oe over the temperature range 2–300 K (Supplementary Figs. S40–S49). Compounds **3**, **9** and **10** could not be separated from paramagnetic impurities and consequently were not studied. The magnetic data for compounds **1**, **2**, **5–8**, **11** and **13** conformed to simple Curie–Weiss behavior. A temperature-independent paramagnetism term (TIP) was added to take into account the baseline correction. The final expression used to fit the susceptibility data was the following:

$$\chi = \chi_h + TIP = \frac{Ng^2 \mu_B^2 S(S+1)}{3k_B [T-\theta]} + TIP$$
(1)

As a function of the effective magnetic moment:

$$\chi = \chi_h + \text{TIP} = \frac{\mu_{\text{eff}}^2}{8[T - \theta]} + TIP$$
(2)

where

 $\mu_{\rm eff}^2 = g^2 S(S+1).$

Compound **6** gives characteristic best fit values for μ_{eff}^2 , θ and g of 1.90 ± 0.25, -0.27 ± 0.09 and 2.12, respectively, which are consistent with d⁹-Cu(II) sites (*S* = 1/2).

In contrast, compounds **2**, **4** and **12** exhibit χ vs. *T* plots indicative of low temperature magnetic ordering (Fig. 14). The plots for compounds **4** and **12** exhibit distinct maxima below 50 K and θ values of -13.4 and -36.7, respectively, suggesting antiferromagnetic coupling between the copper(II) sites. The magnetic behaviors of these latter compounds exhibit significant field dependences. The contrasting behavior of the magnetic properties

Table 3

Selected structural features for the copper-phosphonates of this study and of representative copper-phosphonates.

Compound	Dimensionality	Cu coordination	Phosphonate coordination	Reference
(a) Aromatic di- and triphosphonate				
$[Cu_2(H_2O)_2(O_3PC_8H_8PO_3)] (1)$	3-D	{CuO ₅ } square	One terminus bridges 3 Cu	This work
$[Cu(H_2O)(o-phen)(HO_3PC_8H_8PO_3H)]\cdot 3H_2O (2\cdot 3H_2O)$	Molecular	{CuN ₂ O ₃ } square planar	One terminus bridges two Cu sites, one is pendant	This work
$[Cu_2(H_2O)_2(o-phen)_2(O_3PC_8H_8PO_3)]\cdot 6H_2O\;(\textbf{3}\cdot 6H_2O)$	1-D	{CuN ₂ O ₃ } square	Each terminus bridges two	This work
$[Cu(o-phen)(HO_3PC_8H_8PO_3H)]\cdot 3H_2O (4\cdot 3H_2O)$	2-D	fanar {CuN ₂ O ₃ } square planar	One terminus bridges two Cu sites, one bridges one Cu	This work
$[Cu(o-phen)(HO_3PC_8H_8PO_3H)]$ (5)	2-D	{CuN ₂ O ₃ } square planar	One terminus bridges two Cu sites, one bonds to one	This work
$[Cu(o-phen)(HO_3PC_8H_8PO_3H)] (6)$	1-D	{CuN ₂ O ₃ } square planar	One terminus bridges two Cu sties, one bonds to one	This work
$[Cu_2(H_2O)_2(bpy)_2(HO_3PC_8H_8PO_3H_2)_2(HO_3PC_8H_8PO_3H)]\cdot 2H_2O(\textbf{7}\cdot 2H_2O)$	Molecular	{CuN ₂ O ₃ } square	One terminus bridges to	This work
$[Cu(bpy)(HO_3PC_8H_8PO_3H)]\cdot 2H_2O (8\cdot 2H_2O)$	2-D	fanar {CuN ₂ O ₃ } square planar	One terminus bridges two Cu sites, one bonds to one Cu site	This work
$[Cu(bpy)(HO_3PC_8H_8PO_3H)]$ (9)	1-D	{CuN ₂ O ₃ } square planar	One terminus bridges two Cu sites, one bonds to one Cu site	This work
$\label{eq:cu2} \begin{split} & [Cu_2(H_2O)_2(tpypyz)(H_2O_3PC_8H_8PO_3H)_2(HO_3PC_8H_8PO_3H)]\cdot(H_2O_3PC_8H_8PO_3H_2)_2\cdot 2H_2O \\ & (10\cdot(H_2O_3PC_8H_8PO_3H_2)_2\cdot 2H_2O) \end{split}$	1-D	{CuN ₂ O ₄ } distorted octahedron	One terminus bridges two Cu sites, one terminus is pendant, one is uncoordinated	This work
$[Cu_{2}(tpypyz)(HO_{3}PC_{8}H_{8}PO_{3}H)_{2}]\cdot 2H_{2}O (11\cdot 2H_{2}O)$	Molecular	{CuN ₂ O ₃ } square	One terminus bridges one	This work
[Cu ₄ (Cl) ₄ (tpypyz) ₂ (H ₂ O ₃ PC ₈ H ₈ PO ₃ H) ₂]Cl ₂ ·H ₂ O ₃ PC ₈ H ₈ PO ₃ H ₂ ·8H ₂ O (12 .H ₂ O ₃ PC ₈ H ₈ PO ₃ H ₂ ·8H ₂ O)	Molecular	{CuN ₃ OCl} square planar	One terminus bridges two Cu sites, one is pendant	This work
$[Cu(2,2'dipyidylamine)(HO_3PC_8H_8PO_3H)] (13)$	Molecular	{CuN ₂ O ₂ } tetrahedral	One terminus bridges two Cu sites, one is pendant	This work
$[Cu(ophen){HO_3P(C_{12}H_8)PO_3H}]$	Molecular	{CuO ₂ N ₂ } square planar	Each terminus bonds to a single Cu site	[47]
$[{Cu(ophen)}_{2}{HO_{3}P(C_{12}H_{8})PO_{3}H}]$	Molecular	{CuON ₂ } Cu(I), "T" shaped	Each terminus bonds to a single Cu site	[47]
$[Cu(terpy){HO_3P(C_{12}H_8PO_3H)]}\cdot H_2O$	1-D	${CuO_3N_2}$ '4+1' type	Each terminus bonds to a single Cu site	[47]
$Cu(HO_3PCH_2)_2C_6H_4[N(CH)_4CC(CH)_4N]\cdot 2H_2O$	2-D	{CuO ₄ N ₂ } distorted octahedron	Each terminus bonds to a single Cu Site	[61]
$Cu(HO_3PCH_2)_2C_6H_4[N(CH)_4CC(CH)_4N]\cdot 2H_2O$	2-D	{CuO ₄ N ₂ } distorted octahedron	Each terminus bonds to a single Cu Site	[61]
(b) Aliphatic diphosphonates with secondary nitrogen-donor ligands $[Cu_3(HL)_2(Hpyterpy)_2]\cdot 2H_2O HL_5 = 1-hydroxyethylidenediphosphonic acid$	3-D	{CuO ₃ N} distorted tetrahedral and {CuO4N} square	Two termini bridge 3 Cu sites and two termini bridge two Cu sites	[62]
$[Cu_4(HL)_2(4,4'-bipy)(H_2O)_5]$ HL ₅ = 1-hydroxyethylidenediphosphonic acid	2-D	planar {CuNO ₄ } and {CuO ₅ } square	One terminus bridges 3 Cu sites, one terminus bridges	[62]
$[Cu(bpy){HO_3P(CH_2)_3PO_3H}]$	2D	planar {CuO₃N} square pyramids	two Cu sites One terminus bridges 2 Cu sites; the second bonds to a	[36]
$[Cu(4,4'-bpy)(H_2O)_2{HO_3P(CH_2)_4PO_3H}]$	2D	$[CuO_4N_2]$ '4+2'	Each terminus bonds to a single Cu site	[36]
$[{Cu(phen)(H_2O)}_2(O_3PCH_2CH_2PO_3)]$	Molecular	{Cu(O_3N_2 } square	Each terminus chelate a Cu site	[37]
[Cu(terpy)(HO ₃ PCH ₂ CH ₂ PO ₃ H)]	1-D	{CuO ₂ N ₃ } square	Each terminus bonds to a single Cu site	[37]
$[Cu(mephenterpy){HO_{3}P(CH_{2})_{4}PO_{3}H}]$	1-D	${CuO_2N_3}$ square pyramids	Each terminus bonds to a single Cu site	[39]

of compounds **2**, **4** and **12** and the other compounds of this study presumably reflects the different overlaps and orientations of the magnetic orbitals. However, since the fitting of the magnetic data for compounds **2**, **4** and **12** requires further investigation, the interpretation of the trends in the magnetism of these compounds remains speculative. These preliminary magnetic investigations will be expanded upon in future communications in light of field dependent studies.

4. Conclusions

Hydrothermal synthesis has been used to prepare thirteen new copper-organodiphosphonate compounds. The parent compound $[Cu_2(H_2O)_2(1,4-O_3PC_8H_8PO_3)]$ (1) exhibits the common pillared layer structure. The remaining compounds incorporate organoimine chelates to occupy coordination sites on the copper centers in order to reduce the dimensionality of the resultant copper(II)/

xylyl-diphosphonate/chelate materials. While this end was achieved, the structural details proved diverse and unpredictable Table 3.

Of the *o*-phenthroline derivatives, compounds **4** and **5** are twodimensional, **3** and **6** are one-dimensional and **2** is molecular. For the 2,2'-bipyridyl analogues, **8** is two-dimensional while **9** is onedimensional and **7** is molecular. Most curiously, the tetra-2-pyridylpyrazine derivatives provide a one-dimensional material **10** and two molecular species **11** and **12**. In view of the bridging coordination generally adopted by tpyprz, we had naively assumed that copper-diphosphonate chains linked through tpyprz rods into 2-D or even 3-D structures would predominate.

The unpredictability of the structures reflects a number of structural determinants. The coordination geometry of the copper is variable with '4+1' and '4+2' axially distorted geometries and even square planar geometry making regular appearances. Variable aqua coordination is also common. The organophosphonate ligands can coordinate in a variety of ways and can display different degrees of protonation. Pendant $-PO_3$ termini are not uncommon and a given $-PO_3$ terminus can bond to one to four metal sites. Finally the identity of the tether of the diphosphonate ligand can also serve as a structural determinant; that is, it does not function solely as an innocent spacer.

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Appendix A. Supplementary material

CCDC 881705–881717, comprises the final atomic coordinates for all atoms, thermal parameters, and a complete listing of bond distances and angles, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http:// www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.ica.2013.01.001.

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