

Syntheses, Structures, and Magnetic Properties of Inorganic–Organic Hybrid Cobalt(II) Phosphites Containing Bifunctional Ligands

Jian Fan, Gordon T. Yee, Guangbin Wang, and Brian E. Hanson*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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Seven new cobalt(II) phosphites, $[\text{Co}(\text{HPO}_3)(\text{C}_{14}\text{H}_{14}\text{N}_4)(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Co}(\text{HPO}_3)(\text{C}_{22}\text{H}_{18}\text{N}_4)]\cdot \text{H}_2\text{O}$ (**2**), $[\text{Co}_2(\text{HPO}_3)_2(\text{C}_{22}\text{H}_{18}\text{N}_4)_2\text{H}_2\text{O}]\cdot \text{H}_2\text{O}$ (**3**), $[\text{Co}_2(\text{HPO}_3)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)_{1.5}\text{H}_2\text{O}]\cdot 1.5\text{H}_2\text{O}$ (**4**), $[\text{Co}(\text{HPO}_3)(\text{C}_{14}\text{H}_{14}\text{N}_4)_{0.5}]\cdot \text{H}_2\text{O}$ (**5**), $[\text{Co}(\text{HPO}_3)(\text{C}_{18}\text{H}_{16}\text{N}_4)_{0.5}]$ (**6**), and $[\text{Co}(\text{HPO}_3)(\text{C}_{18}\text{H}_{16}\text{N}_4)_{0.5}]$ (**7**) were synthesized in the presence of 1,2-bis(imidazol-1-ylmethyl)benzene (L1), 1,4-bis(benzimidazol-1-ylmethyl)benzene (L2), 1,3-bis(benzimidazol-1-ylmethyl)benzene (L3), 1,4-bis(1-imidazolyl)benzene (L4), 1,4-bis(imidazol-1-ylmethyl)benzene (L5), 1,4-bis(imidazol-1-ylmethyl)naphthalene (L6), and 1,5-bis(imidazol-1-ylmethyl)naphthalene (L7), respectively, and their structures were determined by X-ray crystallography. Compound **1** is a molecular compound in which two cobalt(II) ions are held together by double μ -O linkages. The inorganic framework of compounds **2** and **3** are composed of vertex-shared $\text{CoO}_2\text{N}_2/\text{CoO}_3\text{N}_2$ and HPO_3 polyhedra that form four rings; these are further linked by an organic ligand to generate 2D sheets. Compounds **4** and **5** both have 1D inorganic structures, with the bifunctional ligands connected to each side of the ladder by coordination bonds to give 2D hybrid sheets. A 3D organically pillared hybrid framework is observed in **6** and **7**. In **6**, the stacking of the interlayer pillars gives rise to a small hydrophobic channel that extends through the entire structure parallel to the sheets. The temperature-dependent magnetic susceptibility measurements of these compounds show weak interactions between the metal centers, mediated through the μ -O and/or O–P–O linkages.

Introduction

Metal phosphate/phosphite compounds have attracted substantial research interest primarily because of their structural features, which lead to their potential applications in the areas of ion exchange, membranes, nonlinear optics, and catalysis.¹ Among these compounds, zinc phosphates and zinc phosphites, ZnPOs, have been extensively studied. Generally, there are three strategies to prepare these compounds: (i) hydrothermal synthesis in the presence of a structure-directing agent such as a template;² (ii) the use of an organophosphate to construct hybrid frameworks;³ and (iii) the use of organic ligands as structure-building units

independent of the phosphate/phosphite group to obtain inorganic–organic networks.⁴ In contrast to the ZnPOs, the analogous CoPOs have not been studied as extensively. In the past decade, CoPO materials have been synthesized mainly by the first two methods listed above.⁵ For example, Rao and co-workers reported the synthesis of layered cobalt phosphates with amine templates, which provides a facile pathway to open-framework cobalt phosphates,⁶ and Zheng

* To whom correspondence should be addressed. E-mail: hanson@vt.edu.

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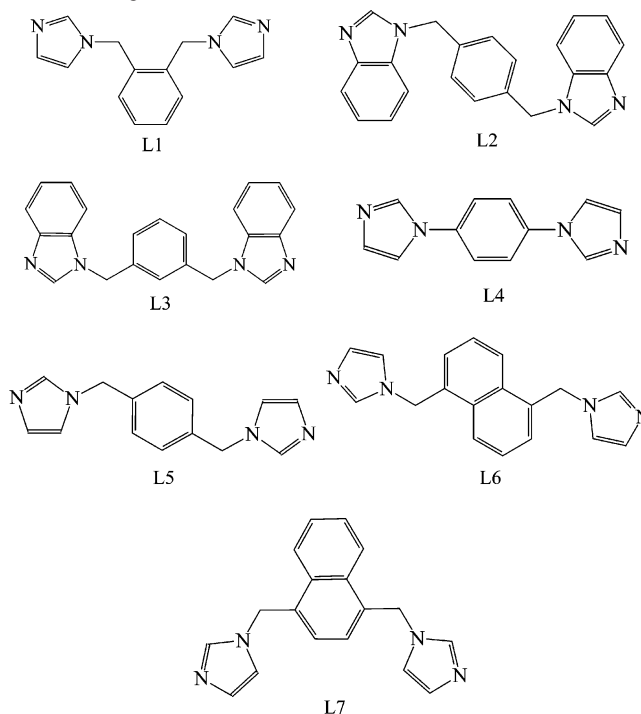
et al. systematically explored the synthesis and magnetic properties of CoPOs that incorporate organophosphate ligands into the hybrid structure.⁷ However, the preparation of hybrid CoPOs in which the inorganic building units are further linked by nitrogen donor ligands has not been fully exploited.⁸

Recent efforts on the cobalt materials have focused on the potentially interesting magnetic properties of the CoPOs. For example, the compound $[\text{enH}_2][\text{Co}_{3.5}(\text{PO}_4)_3]$ has a channel structure and exhibits a structural change accompanied by the development of ferrimagnetism at low temperature.⁹ From a synthetic point of view, organic ligands provide the opportunity to tailor the inorganic aggregation, by means of connection or separation of the building units, to achieve interesting inorganic motifs.⁴ From a magnetic point of view, the organic–inorganic compounds provide the possibility of new magnetic materials by the selection of appropriate bridging ligands.⁸ In this paper, we report the syntheses, crystal structures, and magnetic properties of seven inorganic–organic hybrid cobalt phosphites containing the bifunctional ligands shown in Chart 1.

Experimental Section

Materials and Measurements. All commercially available chemicals were of reagent grade and were used as received without further purification. The ligands 1,2-bis(imidazol-1-ylmethyl)benzene (L1),¹⁰ 1,4-bis(benzimidazol-1-ylmethyl)benzene (L2),¹¹ 1,3-bis(benzimidazol-1-ylmethyl)benzene (L3),¹² 1,4-bis(1-imidazolyl)benzene (L4),¹³ 1,4-bis(imidazol-1-ylmethyl)benzene (L5),¹⁴ 1,4-bis(imidazol-1-ylmethyl)naphthalene (L6),¹⁵ and 1,5-bis(imidazol-1-ylmethyl)naphthalene (L7)¹⁵ were synthesized by literature procedures. Elemental analyses of C, H, and N were performed by Galbraith Laboratories, Inc. Thermogravimetric analysis (TGA) measurements were performed on a TGA Q500 thermal analyzer in flowing N_2 with a heating rate of $10^\circ\text{C min}^{-1}$. TGA curves are shown in the Supporting Information. All of the magnetic measure-

Chart 1. Ligands L1–L7



ments were performed on a 7-T Quantum Design MPMS SQUID magnetometer. Measurements of magnetization as a function of the temperature were performed from 1.8 to 300 K at an applied field of 5000 G.

[Co(HPO₃)(C₁₄H₁₄N₄)(H₂O)₂·2H₂O (1). A mixture of cobalt(II) fluoride (29.1 mg, 0.3 mmol), phosphorus acid (49.2 mg, 0.6 mmol), sodium hydroxide (20.0 mg, 0.5 mmol), 1,2-bis(imidazol-1-ylmethyl)benzene (107.1, 0.45 mmol), and distilled water (20 mL) was stirred for 5 min and then was allowed to stand for 2 days at room temperature to yield a pink crystalline product. Yield: 89% on the basis of cobalt(II) fluoride. FT-IR (cm^{-1}): 3133(w), 2378(w), 1517(m), 1409(m), 1277(m), 1240(m), 1102(s), 1083(s), 1047(m), 1027(s), 962(m), 940(s), 843(s), 760(m), 717(s), 670(m). Anal. Calcd for C₁₄H₂₃CoN₄O₇P: C, 37.43; H, 5.16; N, 12.47. Found: C, 37.16; H, 5.41; N, 12.32. The weight loss by TGA from 25 to ca. 115 °C corresponds to the loss of water molecules (obsd, 15.8%; 4H₂O calcd, 16.0%); no appreciable further weight loss was observed up to 219 °C; the total weight loss at 500 °C was 49%, which corresponds to partial degradation of the ligand.

[Co(HPO₃)(C₂₂H₁₈N₄)·H₂O (2). Hydrothermal treatment of cobalt(II) fluoride (29.1 mg, 0.3 mmol), phosphorus acid (24.6 mg, 0.3 mmol), sodium hydroxide (10.0 mg, 0.25 mmol), 1,4-bis(benzimidazol-1-ylmethyl)benzene (101.4 mg, 0.3 mmol), and water (6 mL) for 10 days at 130 °C yields a blue crystalline product. Yield: 67% on the basis of the cobalt source. FT-IR (cm^{-1}): 3091(w), 2345(w), 1612(m), 1507(m), 1481(m), 1386(m), 1261(m), 1191(m), 1128(s), 1078(s), 1019(m), 1003(s), 969(s), 944(m), 767(s), 759(s), 737(m). Anal. Calcd for C₂₂H₂₁CoN₄O₄P: C, 53.34; H, 4.27; N, 11.31. Found: C, 53.26; H, 4.50; N, 11.25. The weight loss from 23 to ca. 127 °C corresponds to the loss of water molecules (obsd, 3.3%; 1H₂O calcd, 3.6%). This compound is stable up to 275 °C, as shown in the TGA curve; an additional loss of 55% is observed by 600 °C, which corresponds to near complete loss of the ligand.

[Co₂(HPO₃)₂(C₂₂H₁₈N₄)₂H₂O]·H₂O (3). Hydrothermal treatment of cobalt(II) fluoride (29.1 mg, 0.3 mmol), phosphorus acid (49.2 mg, 0.6 mmol), sodium hydroxide (20.0 mg, 0.5 mmol), 1,3-bis-

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Table 1. Crystal Data and Structure Refinement Parameter for 1–7

parameter	structure			
	1	2	3	4
empirical formula	C ₂₈ H ₄₆ Co ₂ N ₈ O ₁₄ P ₂	C ₂₂ H ₂₁ CoN ₄ O ₄ P	C ₄₄ H ₄₂ Co ₂ N ₈ O ₈ P ₂	C ₁₈ H ₂₂ Co ₂ N ₆ O _{8.5} P ₂
fw	898.53	495.33	990.66	638.22
T/K	100	100	100	100
space group	P2 ₁ /c	P $\bar{1}$	P2 ₁ /n	C2/c
a/Å	13.3004(10)	10.1338(10)	8.5992(7)	28.245(4)
b/Å	11.2986(9)	10.5093(10)	23.2386(18)	11.8501(16)
c/Å	12.6370(10)	11.1176(10)	20.7890(12)	17.263(3)
α /deg		71.871(8)		
β /deg	99.339(7)	78.973(8)	98.961(6)	126.80(3)
γ /deg		86.705(8)		
V/Å ³	1873.9(3)	1104.46(18)	4103.6(5)	4626.3(12)
Z	2	2	4	8
D _{calcd} /g cm ⁻³	1.592	1.489	1.603	1.833
μ /mm ⁻¹	1.046	0.886	0.954	1.635
R1 ^a [I > 2 σ (I)]	0.0406	0.0424	0.0582	0.0639
wR2 ^b [I > 2 σ (I)]	0.0919	0.1130	0.1180	0.1442

structure parameter	structure		
	5	6	7
empirical formula	C ₇ H ₁₀ CoN ₂ O ₄ P	C ₉ H ₉ CoN ₂ O ₃ P	C ₉ H ₉ CoN ₂ O ₃ P
fw	276.07	283.08	283.08
T/K	100	100	100
space group	P2 ₁ /n	C2/c	C2/c
a/Å	11.173(2)	24.250(3)	23.535(5)
b/Å	5.2242(9)	9.3609(9)	9.1145(11)
c/Å	17.6690(19)	9.9408(9)	9.8127(19)
β /deg	100.432(12)	94.973(13)	91.56(3)
V/Å ³	1014.3(3)	2248.0(4)	2104.1(6)
Z	4	8	8
D _{calcd} /g cm ⁻³	1.808	1.673	1.787
μ /mm ⁻¹	1.844	1.660	1.774
R1 ^a [I > 2 σ (I)]	0.0509	0.0391	0.0645
wR2 ^b [I > 2 σ (I)]	0.1313	0.1118	0.1636

^a R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^b wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [(F_o)^2 + 2(F_c)^2]/3$.

(benzimidazol-1-ylmethyl)benzene (101.4 mg, 0.3 mmol), and water (6 mL) for 9 days at 130 °C yields a blue crystalline product. Yield: 73% on the basis of the cobalt source. FT-IR (cm⁻¹): 3096(w), 2336(w), 1611(m), 1520(m), 1509(m), 1435(m), 1389(m), 1299(m), 1271(m), 1158(s), 1047(s), 1017(m), 974(s), 917(m), 759(s), 750(s), 743(s). Anal. Calcd for C₄₄H₄₂Co₂N₈O₈P₂: C, 53.34; H, 4.27; N, 11.31. Found: C, 53.68; H, 4.56; N, 11.40. The weight loss from 35 to ca. 175 °C corresponds to the loss of water molecules (obsd, 3.7%; 2H₂O calcd, 3.6%). This compound is stable up to 250 °C, as shown in the TGA curve. From 250 to 425 °C, an additional 65% of the mass is lost. This corresponds closely to the complete loss of the ligand, 64.6%.

[Co₂(HPO₃)₂(C₁₂H₁₀N₄)_{1.5}H₂O]·1.5H₂O (4). Hydrothermal treatment of cobalt(II) fluoride (29.1 mg, 0.3 mmol), phosphorus acid (49.2 mg, 0.6 mmol), sodium hydroxide (20.0 mg, 0.5 mmol), 1,4-bis(1-imidazolyl)benzene (63.0 mg, 0.3 mmol), and water (6 mL) for 9 days at 130 °C yields a blue crystalline product. Yield: 63% on the basis of the cobalt source. FT-IR (cm⁻¹): 3106(w), 2357(w), 1528(s), 1496(m), 1308(m), 1265(m), 1253(m), 1134(s), 1101(s), 1071(s), 1036(s), 1019(s), 958(s), 940(s), 835(s), 737(s). Anal. Calcd for C₁₈H₂₂Co₂N₆O_{8.5}P₂: C, 33.88; H, 3.47; N, 13.17. Found: C, 34.16; H, 3.57; N, 13.16. The weight loss from 25 to ca. 170 °C corresponds to the loss of water molecules (obsd, 7.1%; 2.5H₂O calcd, 7.1%). From 170 to 400 °C, additional weight is lost in three stages for a total of 44%, which exceeds the mass of the ligand.

[Co(HPO₃)(C₁₄H₁₄N₄)_{0.5}]·H₂O (5). Hydrothermal treatment of cobalt acetate tetrahydrate (249.1 mg, 1 mmol), phosphorus acid (82 mg, 1 mmol), 1,4-bis(imidazol-1-ylmethyl)benzene (238 mg,

1 mmol), water (2 mL), and *N,N*-dimethylformamide (4 mL) for 13 days at 90 °C yields a blue crystalline product. Yield: 51% on the basis of the cobalt source. FT-IR (cm⁻¹): 3117(w), 2413(w), 1639(m), 1527(m), 1444(m), 1400(w), 1360(w), 1250(m), 1131(s), 1106(s), 1098(s), 1076(s), 1027(s), 998(s), 952(s), 863(m), 782(s). Anal. Calcd for C₇H₁₀CoN₂O₄P: C, 30.45; H, 3.65; N, 10.15. Found: C, 30.52; H, 3.97; N, 9.99. The weight loss (29–117 °C) corresponds to the loss of water molecules (obsd, 6.4%; 1H₂O calcd, 6.5%). This compound is stable up to 340 °C, as shown in the TGA curve. From 340 to 425 °C, an additional 19% of the mass is lost. This corresponds to a small fraction of the mass percent of the ligand in the sample, 86%.

[Co(HPO₃)(C₁₈H₁₆N₄)_{0.5}] (6). Hydrothermal treatment of cobalt acetate tetrahydrate (249.1 mg, 1 mmol), phosphorus acid (82 mg, 1 mmol), 1,4-bis(imidazol-1-ylmethyl)naphthalene (288 mg, 1 mmol), water (2 mL), and *N,N*-dimethylformamide (4 mL) for 13 days at 90 °C yields a blue crystalline product. Yield: 84% on the basis of the cobalt source. FT-IR (cm⁻¹): 3106(w), 2363(w), 1519(m), 1457(w), 1404(w), 1281(w), 1238(w), 1141(m), 1092(s), 1082(s), 1032(s), 1007(s), 948(m), 867(m), 794(m), 738(s). Anal. Calcd for C₉H₉CoN₂O₃P: C, 38.19; H, 3.20; N, 9.89. Found: C, 38.21; H, 3.50; N, 9.88. The TGA of 6 shows negligible weight loss up to 425 °C. From 425 to 450 °C, the sample loses 35% of its mass. This corresponds to a loss of over half of the ligand present in the sample.

[Co(HPO₃)(C₁₈H₁₆N₄)_{0.5}] (7). Hydrothermal treatment of cobalt acetate tetrahydrate (249.1 mg, 1 mmol), phosphorus acid (82 mg, 1 mmol), 1,4-bis(imidazol-1-ylmethyl)naphthalene (216 mg, 0.75 mmol), and water (6 mL) for 10 days at 130 °C yields a blue

crystalline product. Yield: 81% on the basis of the cobalt source. FT-IR (cm⁻¹): 3102(w), 2400(w), 1528(m), 1446(w), 1345(w), 1289(m), 1254(m), 1142(s), 1100(s), 1079(s), 1039(s), 1027(s), 1004(s), 947(m), 879(m), 848(m), 735(s). Anal. Calcd for C₉H₉CoN₂O₃P: C, 38.19; H, 3.20; N, 9.89. Found: C, 38.26; H, 3.42; N, 9.86. The TGA of **7** shows negligible weight loss up to 425 °C. From 425 to 450 °C, the sample loses 32% of its mass. This corresponds to a loss of over half of the ligand present in the sample.

Crystallographic Analyses. Low-temperature (100 K) single-crystal X-ray diffraction measurements for complexes **1–7** were collected on a Oxford Diffraction Xcalibur2 diffractometer equipped with the Enhance X-ray source and a Sapphire 2 CCD detector. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlis.¹⁶ The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares.¹⁷ The final refinements involved an anisotropic model for all non-hydrogen atoms. One hydrogen atom bonded to the lattice water oxygen O3W in compound **4** was not located. All other hydrogen atoms were either located from the residual e⁻ density map and refined independently or located by a riding model. The crystal parameters, data collection, and refinement results for compounds **1–7** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Results and Discussion

Description of the Crystal Structures of [Co(HPO₃)(C₁₄H₁₄N₄)(H₂O)₂]·2H₂O (1**), [Co(HPO₃)(C₂₂H₁₈N₄)·H₂O (**2**), and [Co₂(HPO₃)₂(C₂₂H₁₈N₄)₂·H₂O (**3**).** The asymmetric unit of compound **1** contains one cobalt(II) cation, one phosphite anion, one L1 unit, two coordinated water molecules, and two lattice water molecules. Each cobalt ion is octahedrally coordinated by two nitrogen atoms from two L1 units, two oxygen atoms from two phosphite anions, and two water oxygens. The coordination angles around the cobalt ion are in the range of 81.04(6)–175.92(6)°, to give a slightly distorted octahedral coordination geometry.

The imidazole groups in the organic ligand of **1** are syn relative to the plane of the benzene ring; that is, the imidazole groups both lie on the same face of the ring. Further, the two imidazole groups within one L1 ligand are nearly parallel to each other with a dihedral angle of 17.7° and a centroid–centroid distance of 3.40 Å. The relatively short distance indicates the existence of a π···π interaction. Two L1 ligands bridge the two cobalt ions, which are further held together by double μ-O linkages to form an edge-shared cobalt dimer. The Co1–Co1A distance is 3.23 Å, and the Co–O–Co angle is 98.96(6)°. The phosphite anions each donate one oxygen atom to generate a planar butterfly structure (Figure 1a, right). Thus, the phosphite anion in **1** adopts a μ₂–η¹ bridging mode in which a single oxygen atom of the phosphite group bridges two cobalt atoms. This arrangement has been seen in some oxovanadium phosphates.¹⁸ The octahedral coordination of each cobalt is completed with trans imidazole groups and two cis water molecules.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1–7**^a

Compound 1			
Co1–N11	2.1116(17)	Co1–O3	2.1161(14)
Co1–N21 ^{#1}	2.1252(17)	Co1–O3 ^{#1}	2.1261(14)
Co1–O5	2.1411(15)	Co1–O4	2.1417(16)
Co1–O3–Co1	98.96	O5–Co1–O4	90.59(6)
O3–Co1–O3 ^{#1}	81.04(6)	N11–Co1–N21 ^{#1}	175.08(7)
Compound 2			
Co1–O1	1.9279(17)	Co1–O3	1.9287(18)
Co1–N4	2.007(2)	Co1–N2	2.024(2)
O1–Co1–O3	117.77(8)	O1–Co1–N4	114.91(8)
O3–Co1–N4	108.87(8)	O1–Co1–N2	106.94(8)
O3–Co1–N2	96.33(8)	N4–Co1–N2	110.27(8)
Compound 3			
Co1–O4	1.922(2)	Co1–O3	1.928(2)
Co1–N111	2.000(3)	Co1–N131	2.025(3)
Co2–O6	1.970(2)	Co2–O2	1.981(2)
Co2–N11	2.048(3)	Co2–N31	2.086(3)
Co2–O7	2.269(2)		
O4–Co1–O3	113.65(10)	O4–Co1–N111	112.95(10)
O3–Co1–N111	119.21(10)	O4–Co1–N131	109.37(10)
O3–Co1–N131	96.84(11)	N111–Co1–N131	102.31(11)
O6–Co2–O2	124.25(10)	O6–Co2–N11	110.19(11)
O2–Co2–N11	124.60(10)	O6–Co2–N31	95.28(10)
N11–Co2–N31	96.74(11)	O2–Co2–O7	88.47(9)
O6–Co2–O7	88.81(10)	N31–Co2–O7	175.78(11)
N11–Co2–O7	82.80(10)		
Compound 4			
Co1–N1	2.109(4)	Co1–N21	2.133(5)
Co1–O7	2.133(4)	Co1–O1	2.144(4)
Co1–O1 ^{#2}	2.149(4)	Co1–O4	2.196(4)
Co2–O3 ^{#2}	1.922(5)	Co2–O5 ^{#3}	1.949(4)
Co2–O4	1.963(4)	Co2–N41 ^{#4}	1.998(5)
Co2–O4–Co1	115.67	Co1–O1–Co1	100.03
Compound 5			
Co1–O3	1.961(3)	Co1–O2	1.915(3)
Co1–O1	1.970(3)	Co1–N1	2.026(4)
O2–Co1–O3	113.79(14)	O2–Co1–O1	111.35(13)
O3–Co1–O1	112.32(13)	O2–Co1–N1	112.28(14)
O3–Co1–N1	103.14(15)	O1–Co1–N1	103.19(14)
Compound 6			
Co1–O1	1.9386(18)	Co1–O3	1.9396(18)
Co1–O2	1.9481(18)	Co1–N1	2.020(2)
O1–Co1–O3	103.94(8)	O1–Co1–O2	105.78(8)
O3–Co1–O2	108.24(8)	O1–Co1–N1	117.11(9)
O3–Co1–N1	112.40(8)	O2–Co1–N1	108.87(8)
Compound 7			
Co1–O2	1.930(4)	Co1–O3	1.934(4)
Co1–O1	1.944(4)	Co1–N1	2.026(5)
O2–Co1–O3	101.31(16)	O2–Co1–O1	113.27(17)
O3–Co1–O1	111.33(17)	O2–Co1–N1	107.72(17)
O3–Co1–N1	115.17(18)	O1–Co1–N1	108.00(17)

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

Each cobalt dimer is connected to four neighboring dimers via two kinds of hydrogen bonds: O4–H4A···O2($x, 3/2 - y, 1/2 + z$) [O4–O2($x, 3/2 - y, 1/2 + z$) = 2.643(2) Å] and O5–H5B···O1($x, 3/2 - y, 1/2 + z$) [O5–O1($x, 3/2 - y, 1/2 + z$) = 2.715(2) Å] to form a 2D sheet in the *bc* plane (Figure 2b). The 2D sheets are held together by van der Waals forces to form a 3D structure along the [100] direction.

The asymmetric unit of compound **2** contains one cobalt(II) cation, one phosphite anion, one L2 ligand, and one lattice water molecule. Each cobalt ion is tetrahedrally coordinated by two nitrogen atoms from two L2 units and

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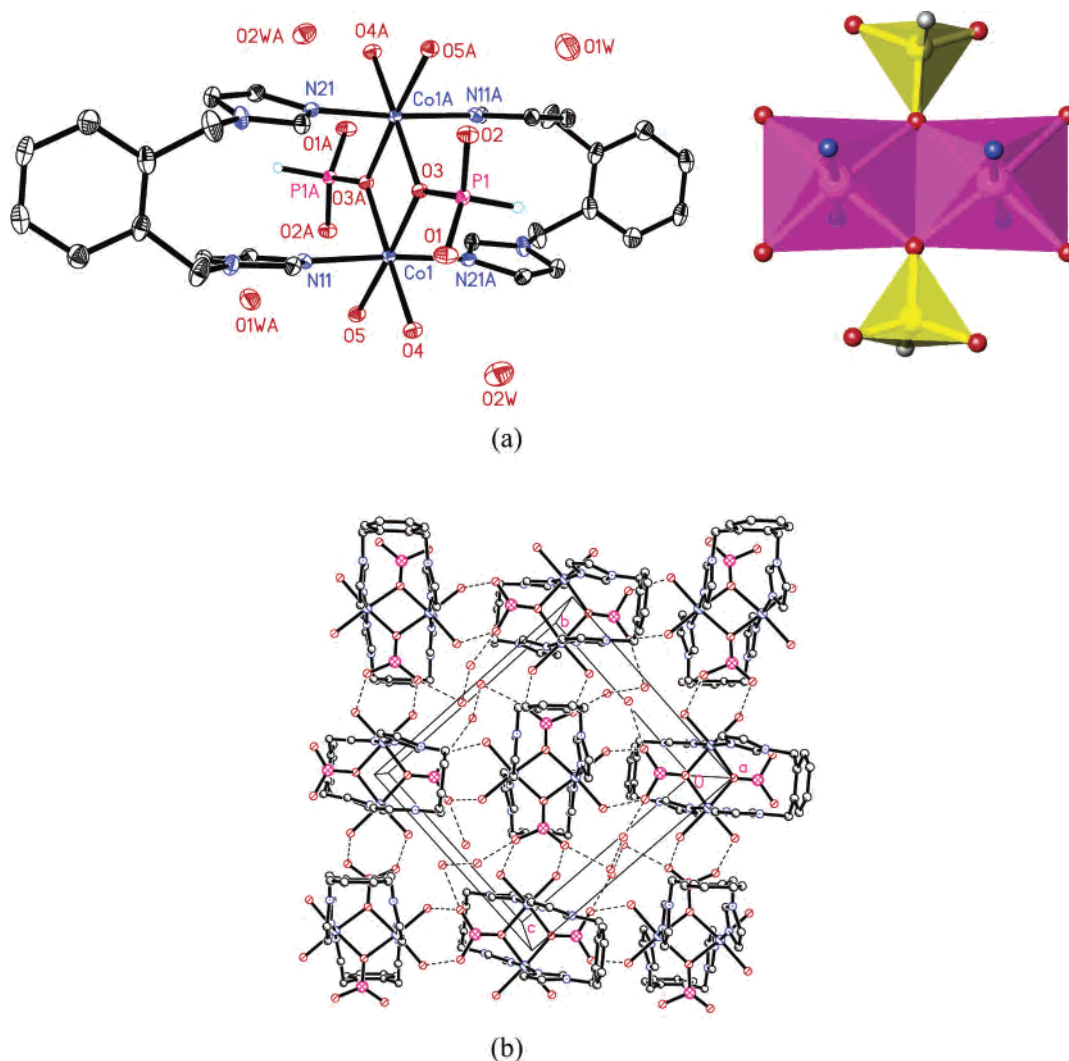


Figure 1. (a) Cobalt dimer with the atom labeling scheme in compound **1**. Thermal ellipsoids are drawn at 50% probability (left). Top view of the cobalt dimer (right). (b) Packing diagram of compound **1** with the hydrogen bonds indicated by dashed lines.

two oxygen atoms from two phosphite anions. The coordination angles around the cobalt ion are in the range of $96.33(8)$ – $117.77(8)^\circ$. Each phosphite anion in **2** adopts the more common μ_2 – η^2 bridging mode. Thus, two cobalt ions and two phosphite anions form the four-ring secondary building unit (SBU; Figure 2a), which is widely observed in related zinc phosphate/phosphite structures.^{4a,b}

In **2**, the benzimidazole groups of L2 adopt an anti conformation. Each four-ring SBU is connected by L2 through the cobalt atoms to form a 2D sheet. If each four-ring is taken as a four-connected node; this 2D sheet has a (4, 4) topology (Figure 2b). Hydrogen bonds are observed between the sheets; these are responsible for the formation of the 3D structure of compound **2**.

In compound **3**, the pendant benzimidazol-1-ylmethyl groups of the organic ligand L3 are at the 1 and 3 positions relative to the central benzene ring, whereas in L2 (in **2**), the same groups are at the 1 and 4 positions. As illustrated in Figure 3a, the asymmetric unit of compound **3** contains two cobalt cations (Co1 and Co2), two phosphite anions (P1 and P2), two L3 ligands, one coordinated water molecule, and one lattice water molecule. The two cobalt atoms have

tetrahedral and trigonal-bipyramidal coordination geometries, respectively; the coordination angles around Co1 are in the range of $96.84(11)$ – $119.21(10)^\circ$, and around Co2, the angles are in the range of $88.47(9)$ – $175.78(11)^\circ$.

Two cobalt cations and two phosphite anions are connected by Co–O–P linkages to generate a four-ring SBU. Within the four-ring, the coordinated water molecule (O7) on Co2 is further stabilized by hydrogen bonds with the neighboring phosphite anions (P1 and P2): $O7-H7A\cdots O1$ [$O7-O1 = 2.653(4)$ Å] and $O7-H7B\cdots O5$ [$O7-O5 = 2.765(4)$ Å].

In **3**, each organic ligand L3 adopts an anti conformation and each phosphite anion adopts a μ_2 – η^2 bridging mode, as observed in **2**. The overall structure of compound **3** is quite similar to that of compound **2** featuring the same 2D hybrid layer with (4, 4) topology (Figure 3b) and hydrogen-bonding interaction between layers.

Compounds $[\text{Co}_2(\text{HPO}_3)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)_{1.5}\text{H}_2\text{O}]\cdot 1.5\text{H}_2\text{O}$ (**4**) and $[\text{Co}(\text{HPO}_3)(\text{C}_{14}\text{H}_{14}\text{N}_4)_{0.5}]\cdot \text{H}_2\text{O}$ (**5**). The asymmetric unit of compound **4** contains two cobalt cations, two phosphite anions, one and a half L4 ligands, one coordinated water molecule, and one and a half lattice water molecules. The first cobalt atom, Co1, is coordinated to three oxygen atoms

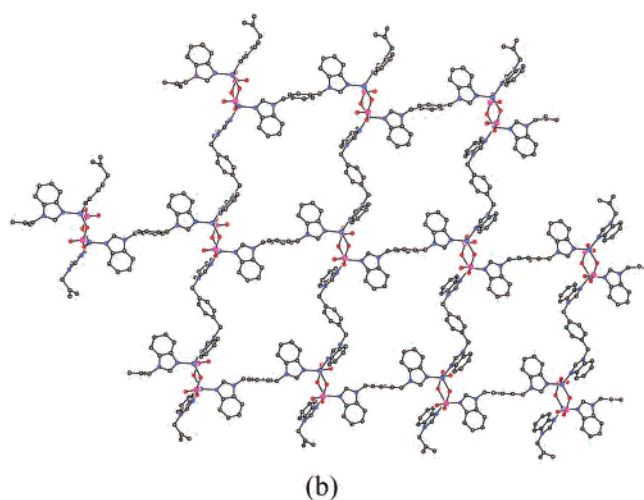
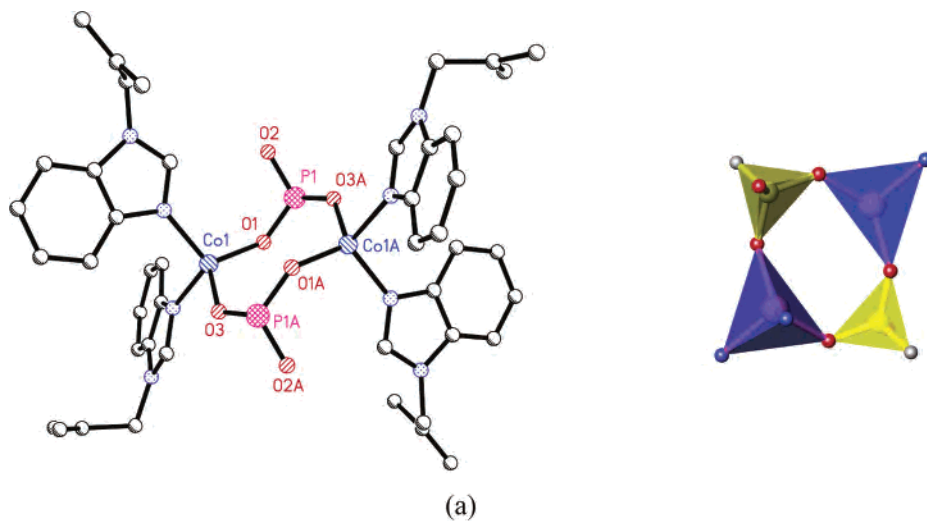


Figure 2. (a) Crystal structure of compound **2** with an atom labeling scheme. Thermal ellipsoids are drawn at 50% probability (left). Polyhedral representation of the four-ring (right). (b) 2D structure of compound **2**.

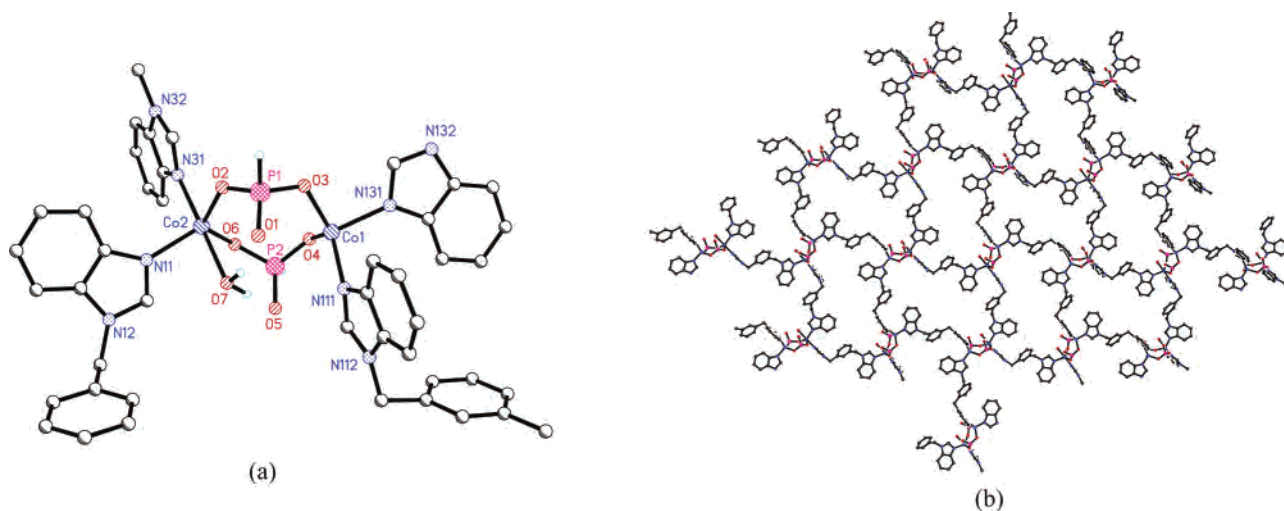


Figure 3. (a) Asymmetric unit of the compound **3** structure showing the atom labeling scheme. Thermal ellipsoids are drawn at 50% probability. (b) 2D structure of compound **3**.

from three phosphite anions, two nitrogen atoms from two L4 ligands, and one water oxygen to give a slightly distorted octahedral geometry with coordination angles in the range of $79.97(16)$ – $176.42(16)^\circ$. As shown in Figure 4a, the two

L4 imidazole groups are trans in **4**. The second cobalt atom, Co2, is tetrahedrally coordinated to three oxygen atoms from three phosphite anions and one nitrogen atom from one L4 ligand. The phosphite anions (P1 and P2) adopt a μ_3 - η^2

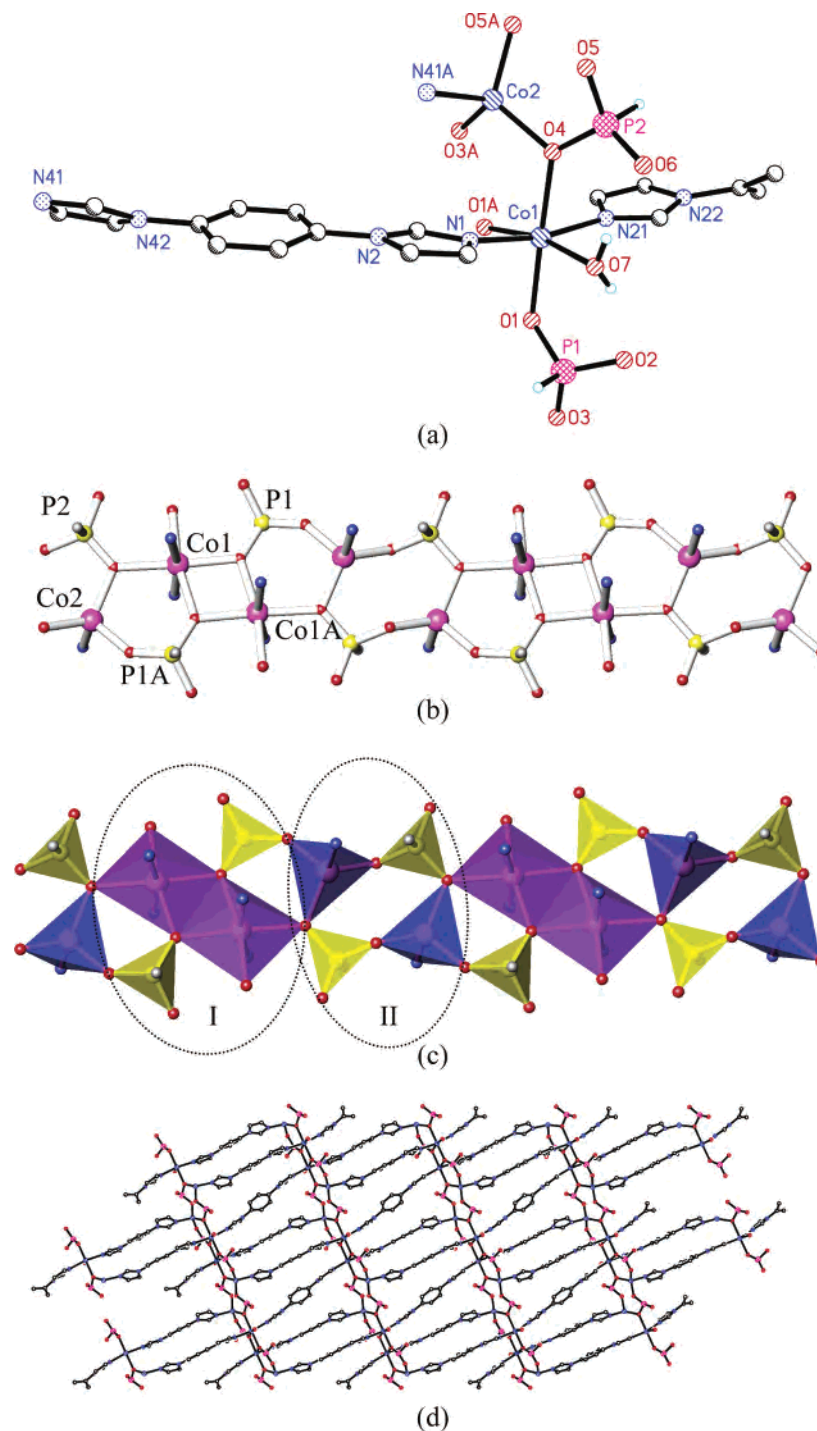


Figure 4. (a) Asymmetric unit of the compound **4** structure showing the atom labeling scheme. Thermal ellipsoids are drawn at 50% probability. (b) 1D inorganic chain in **4** (Co, pink; P, yellow; O, red; N, blue; H, gray). (c) Polyhedral representation of the chain structure in **4** (Co1, purple; Co2, blue; P, yellow). (d) 2D structure of compound **4**.

bridging mode. Thus, each phosphite anion has a free oxygen atom, namely, O2 in phosphite P1 and O6 in phosphite P2, that hydrogen bond to the coordinated water molecule (O7): O7–H7A···O2 [O7–O1 = 2.751(6) Å] and O7–H7B···O6 [O7–O5 = 2.626(6) Å].

In compounds **2** and **3**, the inorganic motifs (four-ring) are isolated, whereas in **4**, a 1D inorganic chain is obtained. The bridging mode between the octahedral and tetrahedral cobalt ions and the phosphite anions leads to a unique ladder structure (Figure 4b). Two familiar units, a dimer and a four-

ring, are labeled I and II, respectively, in Figure 4c. The connection of these units generates a three-ring. Within one chain, the units alternate, dimer, three-ring, four-ring, three-ring, and so on. Within the dimer, the Co1–Co1($\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$) distance is 3.29 Å and the Co–O–Co angle is 100.03(16)°. These parameters are comparable to those in compound **1**. One cobalt octahedron (Co1), one cobalt tetrahedron (Co2), and one phosphorus tetrahedron (P1) are connected through the μ -O and Co–O–P linkages to form a three-ring. Within the three-ring, the Co1–Co2 distance

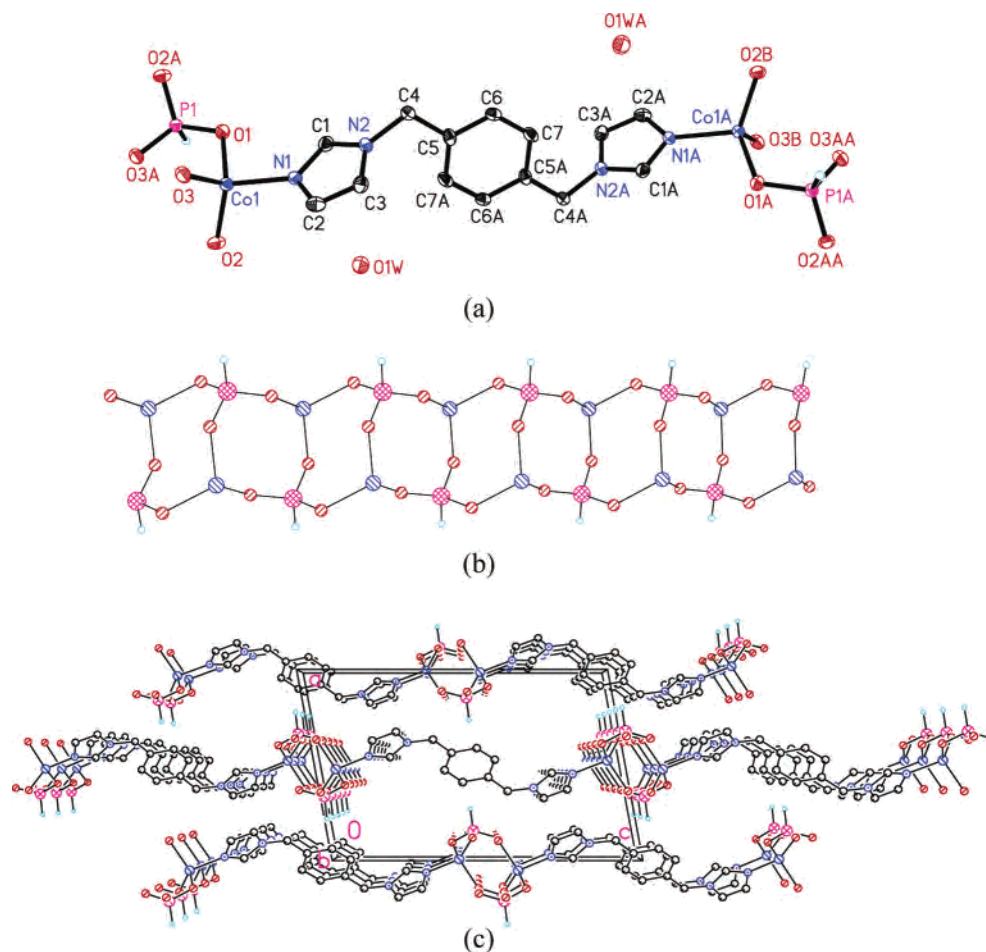


Figure 5. (a) Crystal structure of compound **5** with the atom labeling scheme. Thermal ellipsoids are drawn at 50% probability. (b) 1D inorganic chain in **5** (Co, blue; P, pink; O, red; H, green). (c) Packing diagram of compound **5**.

is 3.52 Å and the Co–O–Co angle is 115.68(18)°. These parameters are larger than those in **1**. Finally, two cobalt tetrahedra (Co2) and two phosphorus tetrahedra (P2) are connected through the Co–O–P linkages to form a four-ring. In **4**, the phosphite anion (P1) that links the two cobalts of the dimer also bridges to a tetrahedral cobalt cation to extend the ladder, whereas in **1**, the bridging phosphite is a terminal pendant group, with respect to the dimer. In **1**, the inorganic dimer terminates with two coordinated water molecules, while in **4**, one water molecule is replaced by the phosphite oxygen of a four-ring to extend the ladder.

As shown in Figure 4c, the inorganic chains are connected by the rigid ligand L4 to generate a 2D structure. Within one layer, all of the chains are parallel to each other. The layers are held together by hydrogen bonding and stack in an AAA mode.

Compared with L4, the ligand L5 is flexible because of the presence of the methylene group between the imidazolyl and central benzene ring. Compound **5** also has a 1D inorganic structure; however, the structural details are different compared to those of **4**.

The asymmetric unit of compound **5** contains one cobalt cation, one phosphite anion, half an L5 ligand, and one lattice water molecule. Each cobalt(II) ion is tetrahedrally coordinated to three oxygen atoms from three phosphite anions and one nitrogen atom from the L5 ligand (Figure 5a). The

coordination angles around the cobalt ion are in the range of 103.14(15)–113.79(14)°, and each phosphite anion adopts a $\mu_3-\eta^3$ bridging mode. The CoO₃N and HPO₃ groups are connected to form an edge-shared ladder structure composed of four rings that propagates along the [010] direction (Figure 5b). This type of ladder is well-known in zinc phosphate and zinc phosphite hybrid structures.⁴

The organic ligand L5 is known to adopt either the syn or anti conformation in its reported coordination compounds.^{4a,b,14} It is notable that in **5** the N2(imidazolyl)–C4(methylene) bonds of L5 lie approximately within the benzene plane with the N2–C4–C5–C6 torsion angle of –168.9(4)°. This conformation appears to be dictated by the hydrogen-bonding interactions between L5 and lattice water as well as a phosphite group from an adjacent ladder: C1–H1D⋯O1W(*x*, –1 + *y*, *z*) [C1–O1W(*x*, –1 + *y*, *z*) = 3.326(6) Å] and C4–H4A⋯O2(1/2 + *x*, 1/2 – *y*, 1/2 + *z*) [C4–O2(1/2 + *x*, 1/2 – *y*, 1/2 + *z*) = 3.289(6) Å].

The inorganic ladders are linked together by L5 to form a 2D structure within the *bc* plane. The 2D sheets are hydrogen bonded along the [100] direction in an ABAB mode to form the 3D structure (Figure 5c).

Compounds [Co(HPO₃)(C₁₈H₁₆N₄)_{0.5}] (**6**) and [Co(HPO₃)(C₁₈H₁₆N₄)_{0.5}] (**7**). The inorganic motifs in compounds **1**–**3** are 0D (dimer and four-ring). In **2** and **3**, the 0D inorganic part is further connected by ligands to form

higher-dimensional hybrid structures. In **4** and **5**, the inorganic portions of the structures are 1D, and these are linked further by organic ligands to form 2D hybrid structures. Compounds **6** and **7** both contain 2D inorganic sheets that are pillared by the organic ligands, L6 and L7, respectively, to form 3D hybrid structures.

The asymmetric unit of compound **6** contains one cobalt atom, one phosphite atom, and half of an L6 ligand, as shown in Figure 6a. Each cobalt atom in compound **6** is coordinated to three oxygen atoms from three different phosphite groups and one nitrogen atom from L6 to complete its tetrahedral coordination environment. The coordination angle around the cobalt ion is in the range of 101.31(16)–113.27(17)°. A similar arrangement is seen in compound **7**. (An equivalent figure for **7** is given in the Supporting Information.)

In compounds **6** and **7**, the cobalt tetrahedra and phosphorus tetrahedra are connected to form a 2D network that has the 4.8² topology,^{4b} as illustrated in Figure 6b for **6**. (An equivalent figure for **7** is given in the Supporting Information.) Within the 4.8² sheet, the cobalt and phosphorus atoms are three-connected through oxygen atoms.

The eight-ring portion of the sheet in **7** is narrower than that in compound **6**. This suggests that the eight-ring is flexible and can adopt a variety of conformations according to the demands of the ligand. In **6**, the L6 ligand adopts a syn conformation with two imidazole groups extending to the same side of the naphthalene ring. The dihedral angle between the imidazole and naphthalene rings is 107.1°. The sheets are connected by L6 ligands to form a pillared 3D structure (Figure 6c). A striking feature of the interlayer pillars is the stacking of the organic ligands to give rise to small hydrophobic channels of dimension 6.0 × 4.7 Å that extend through the entire structure parallel to the sheets. These pores are not accessible to nitrogen gas, as indicated by the nitrogen adsorption isotherm at 77 K. The crystalline material has a Brunauer–Emmett–Teller surface area of 5.2 m² g⁻¹. The distance between the parallel CoPO sheets in **6** is 12.1 Å. In **7**, the N2(imidazolyl)–C4(methylene) bonds lie approximately within the naphthalene plane with the N2–C4–C5–C6 torsion angle of –13.9(8)°. Thus, the L7 ligand adopts an unusual conformation similar to that observed for L5 in compound **5**. This is also attributed to the hydrogen-bonding interactions between the imidazolylmethyl group and neighboring phosphite anions: C1–H1A⋯O1(1/2 – x, –1/2 + y, 3/2 – z) [C1–O1(1/2 – x, –1/2 + y, 3/2 – z) = 3.150(7) Å] and C4–H4B⋯O3(1/2 – x, –1/2 + y, 2 – z) [C4–O3(1/2 – x, –1/2 + y, 2 – z) = 3.301(6) Å]. The sheets in **7** are pillared by L7 ligands to form a 3D structure (the appropriate figure is shown in the Supporting Information); the distance between the parallel CoPO sheets in **7** is 11.8 Å.

Magnetic Properties. The magnetic properties of all of the cobalt complexes in this work are dominated by the expected significant orbital contribution to the magnetic moment^{7,8} and apparent weak antiferromagnetic interactions between Co^{II} centers coupled by O–P–O-bridged phosphite ligands. Compounds **3–7** all exhibit behavior consistent with this characterization. Plots of χT vs T for **3–7** are given in the Supporting Information. The calculated value of spin-

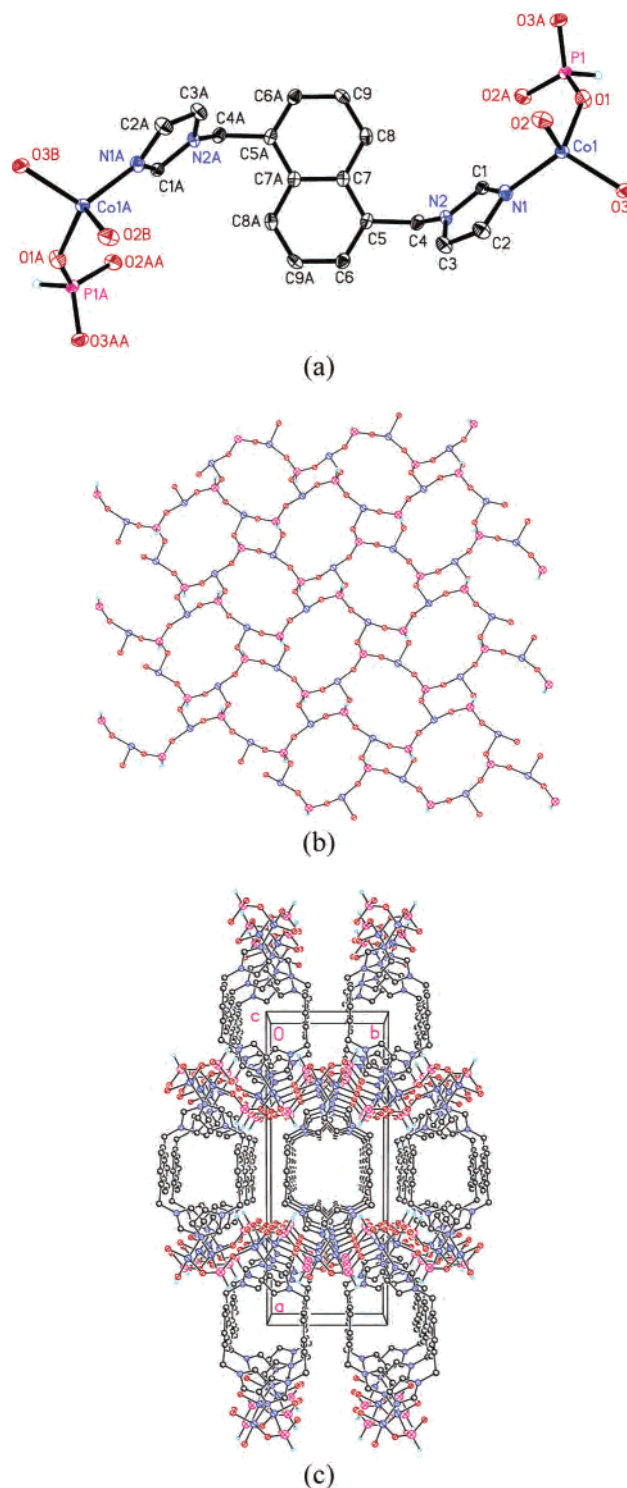


Figure 6. (a) Crystal structure of compound **6** with the atom labeling scheme. Thermal ellipsoids are drawn at 50% probability. (b) 2D hybrid structure of **6** (Co, blue; P, pink; O, red; H, green). (c) Packing diagram of compound **6**.

only χT for $S = 3/2$ and $g = 2$ is 1.875 emu K⁻¹ mol⁻¹ for each metal, and the observed values are between 2.5 and 3.0 emu K⁻¹ mol⁻¹. As the temperature is lowered, χT drops to a low value. It is, however, impossible to deconvolute the effects of spin–orbit coupling, which would also lead to low values of χT .^{5f}

Deviations from this pattern of behavior occur in compounds **1** and **2**. The χT vs T data for compound **1**, which

has μ -O, i.e., a μ_2 - η^1 phosphite bridge, do not drop to low values at low temperature. (The χT vs T plots for all compounds are given in the Supporting Information.) This can be explained by concluding that the bridging μ -O phosphite ligand is not particularly effective at mediating antiferromagnetic coupling. The slight decrease in χT as the temperature is lowered probably reflects the thermal depopulation of states of higher m_s that result from the spin-orbit splitting of the ideal $^4T_{2g}$ ground state, mentioned above.

In the case of compound **2**, χT increases slightly as the temperature is lowered before ultimately tending to a low value. Because the structure of **2** contains the O-P-O-bridged substructure that we believe mediates antiferromagnetic coupling, we hypothesize that slight canting of the moments in this case leads to incomplete cancellation of the moments and thus to the observed behavior. This behavior has been seen previously with Co^{II} bridged by O-P-O diphosphonates.^{5c,7a}

Conclusions

The structural chemistry of ZnPOs is dominated by tetrahedral coordination at zinc. Coordination numbers of five¹⁹ and six²⁰ for zinc in these materials are known but are rare. The most common SBU among the ZnPOs is the four-ring although triple four- and eight-rings are also observed.⁴ Not surprisingly, the structural chemistry of CoPOs also shows a strong preference for tetrahedral coordination. However, there is a greater tendency to higher coordination numbers in Co^{II} compounds compared to Zn^{II} compounds. Among the compounds reported here, coordination numbers of four, five, and six are observed. Because all of the compounds are prepared under similar conditions, the observed coordination numbers may reflect the 3D requirements for the different ligands.

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0D cobalt phosphites are observed in compounds **1–3**; the four-rings of **2**, and **3**, are further linked into 2D hybrid network structures. In compound **4**, a previously unobserved ladder motif is obtained. The ladder differs from the common ZnPO ladder motif that is observed in **5** in that half of the cobalt ions are octahedral and half are tetrahedral in the new ladder. Compounds **6** and **7** contain a planar CoPO phase comprised of a neutral 4.8² network. These are pillared by the bifunctional ligands to form a 3D network. This is a common structural feature of ZnPOs. Compounds **6** and **7** are thermally stable to 425 °C, while compounds **1–5** show significant decomposition after loss of water. We did not observe any transformation of lower-dimensional structures to higher dimensionality in these systems.

The magnetic properties of these compounds are characteristic of Co^{II} with its significant orbital contribution, and the O-P-O linker motif appears to mediate antiferromagnetic coupling between adjacent metal centers. Apparent canting of the antiferromagnetically coupled moments in **2** gives rise to a slight increase in χT with decreasing temperature.

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Supporting Information Available: X-ray crystallographic files, in CIF format, and additional figures for compounds **3–7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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