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## ARTICLE

# Discrete and polymeric cobalt organophosphates: Isolation of a 3-D cobalt phosphate framework exhibiting selective CO<sub>2</sub> capture

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**Abstract:** Structurally diverse mononuclear, dinuclear, and tetranuclear cobalt organophosphates and a three-dimensional framework based on a D4R cobalt phosphate are reported. The role of auxiliary ligands in determining the nuclearity of the phosphate clusters has further been established. Reaction of cobalt acetate tetrahydrate with 2,6-di-*iso*-propylphenylphosphate (dippH<sub>2</sub>) in methanol or DMSO in the presence of ancillary N-donor ligands, leads to the formation of mononuclear octahedral cobalt phosphate [Co(dippH)<sub>2</sub>(py)<sub>4</sub>] (**1**), dinuclear octahedral [Co(dipp)(NN)(MeOH)<sub>2</sub>·2MeOH (NN = bpy **2**; phen **3**), tetrahedral cobalt phosphates [Co(dipp)(L)<sub>2</sub>·2(MeOH) (L = imz **4**; dmpz **5**) and symmetric and asymmetric tetranuclear tetrahedral cobalt phosphates [Co(dipp)(2-apy)<sub>4</sub>] (**6**) and [Co<sub>4</sub>(dipp)<sub>4</sub>(2-apy)<sub>3</sub>(DMSO)]·(DMSO)·(H<sub>2</sub>O) (**7**), in nearly quantitative yields. Use of a linear N-donor ditopic linker 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (dptz) as the ancillary ligand leads to the formation of a robust three dimensional, four-fold interpenetrated network based on the D4R platform, {[Co(dipp)(dptz)<sub>0.5</sub>]<sub>4</sub>}<sub>n</sub> (**8**) at ambient conditions. The new compounds have been characterized by analytical, thermo-analytical and spectroscopic techniques. Further, the molecular structures of compounds **1–8** have been established by single crystal X-ray diffraction studies. Compound **1** is a mononuclear complex in which the dippH ligands occupy trans-positions around the octahedral cobalt ion. The core structure of compounds **2–5**, a Co<sub>2</sub>P<sub>2</sub>O<sub>4</sub> ring, resembles the S4R (single-4-ring) SBU of zeolites, whereas the Co<sub>4</sub>P<sub>4</sub>O<sub>12</sub> inorganic core found in compounds **6** and **7**, resembles the D4R (double-4-ring) SBU. Cobalt organophosphate framework **8** shows significant CO<sub>2</sub> adsorption at 273 K (7.73 wt % at 1 bar and 18.21 wt % at 15.5 bar) with high selectivity to CO<sub>2</sub> uptake over N<sub>2</sub> and H<sub>2</sub> at 273 K. Magnetic studies of these symmetric complexes indicate the presence of weak antiferromagnetic interactions between the metal ions *via* the phosphate bridging moiety.

## Introduction

Capture and storage of CO<sub>2</sub> generated from industrial and energy related sources is one of the major challenges that the scientific community is trying to address in recent times.<sup>1</sup> As per the data of the Intergovernmental Panel on Climate Change, the major contributor to the increase in concentration of anthropogenic greenhouse gas is CO<sub>2</sub> released from the burning of fossil fuels.<sup>2</sup> Further, the Energy Information Administration (EIA) projects that the world's energy consumption will shoot up by 56% between 2010 and 2040.<sup>3</sup> Various methods have been used to adsorb and sequester CO<sub>2</sub>, such as by the use of amines<sup>4</sup> or by adsorption through materials such as activated carbons<sup>5</sup> and zeolites.<sup>6</sup> Recently, metal-organic frameworks (MOFs)<sup>7</sup> and covalent organic frameworks (COFs)<sup>8</sup> have been utilized for this purpose with impressive outcomes. Chemists have designed porous framework materials with nitrogen- or oxygen-containing ligands lining the internal cavities, or with exposed metal sites, and these have shown high CO<sub>2</sub> adsorption due to the enhanced dipole-quadrupole interactions present in such systems.<sup>9</sup> Although a large number of MOFs have been synthesised from various ligands with the goal of improved CO<sub>2</sub> capture properties, frameworks derived from phosphonic acids or

organophosphate esters have not been investigated so far for this purpose.

The synthesis of phosphate analogues of aluminosilicate materials (so-called AIPOs) by Flanigen *et al.*<sup>10</sup> in 1982 inspired exploration other types of zeolite-like phosphate materials.<sup>11</sup> Metallophosphonate layered solids have also been extensively investigated during this period not only because of their structural diversity,<sup>12</sup> but also because of their potential applications in the fields of absorption and separation,<sup>13a</sup> catalysis,<sup>13b,c</sup> photoluminescence,<sup>14</sup> and proton conductivity.<sup>15</sup>

The fact that larger porous architectures can be built rationally from smaller discrete precursors *via* a bottom-up approach further intensified the research on the synthesis of smaller discrete soluble molecular building units based on silicates<sup>16</sup> and phosphates.<sup>11</sup> Due to the presence of two acidic protons and one phosphoryl oxygen, both phosphate esters (RO)P(O)(OH)<sub>2</sub> and phosphonic acids RP(O)(OH)<sub>2</sub> tend to embrace more metal ions around them to form larger aggregates.<sup>11,17</sup> A large number of discrete molecular metallophosphonates and metallophosphates have been synthesised in recent years starting from phosphonic acids<sup>17-21</sup> and phosphate esters,<sup>11,22-24</sup> Much of the recent thrust in metallophosphonate discrete clusters can be attributed their ability to

exhibit interesting magnetic properties,<sup>25,19i</sup> including magnetocaloric effects.<sup>20a-d,27</sup>

In recent years, discrete molecular cage compounds containing cobalt(II) have also attracted large interest due to their potential behaviour as single molecule magnets owing to a large intrinsic magnetic anisotropy due to an unquenched orbital angular momentum.<sup>26</sup> Further, cobalt based phosphate systems have a tendency to act as catalysts particularly for the oxidation of water.<sup>28,29</sup> Although a large number of discrete clusters,<sup>21</sup> as well as layered, pillared, and open framework structures of cobalt organophosphonates are reported in the literature,<sup>30</sup> those of cobalt organophosphates are relatively rare.<sup>30,31</sup>

In view of the aforementioned importance of cobalt phosphates in a variety of applications including catalysis, sorption, and magnetic materials, we have extended our research on metal organophosphate complexes<sup>24</sup> to cobalt based systems, and here we report on the auxiliary ligand assisted structural diversity of cobalt organophosphates based on a phosphate monoester, dippH<sub>2</sub>. This report includes the first example of symmetric and asymmetric D4R zeolitic SBUs based on cobalt organophosphate and the formation of a robust three-dimensional four-fold interpenetrated network based on the D4R platform.

## Experimental Section

### General

The melting points were measured in glass capillaries and are reported uncorrected. Infrared spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer as KBr diluted discs. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyser. Thermogravimetric analysis was carried out on a Perkin Elmer thermal analysis system under a stream of nitrogen gas at a heating rate of 10 °C/min. Gas adsorption measurements were performed on a Quantachrome Autosorb-1C analyser. Magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. The samples were ground to a fine powder, loaded into a gelatin capsule (sample mass ~10 mg), and fixed with frozen eicosane (~20–30 mg). Temperature dependent susceptibility measurements were carried out under static fields of either 0.1 or 0.5 T and over the temperature range 300–2 K. Field dependent magnetisation measurements were carried out between 0–7 T and over the temperature range of 2–4 K. Diamagnetic corrections were applied using a combination of tabulated Pascal constants for the sample diamagnetism, and a subtraction of the sample holder behaviour measured under comparable conditions. Magnetic modelling was performed using PHI software.<sup>32</sup> Single crystal X-ray diffraction data were collected either on an Oxford Xcalibur CCD diffractometer or a Rigaku Saturn724+ diffractometer using MoK $\alpha$  radiation.

### Syntheses

All the compounds prepared in this study are air and moisture stable. Therefore all manipulations were carried out without any rigorous elimination of air or moisture. Solvents were distilled prior to use. Commercially available starting materials such as Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (Sigma Aldrich), pyridine (Merck), 2-aminopyridine (Sigma Aldrich), imidazole (Spectrochem), 2,2'-bipyridine (Sigma Aldrich) and 1,10-phenanthroline (Sigma Aldrich) were used as received. 3,5-Dimethylpyrazole,<sup>33</sup> 2,6-diisopropylphenyl phosphate,<sup>34</sup> and 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine(dptz),<sup>35</sup> were synthesised by following earlier reported procedures.

**[Co(dippH)<sub>2</sub>(py)<sub>4</sub>] (1).** A solution of dippH<sub>2</sub> (129.0 mg, 0.5 mmol) in methanol (10 mL) was added to a solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O

(124.5 mg, 0.5 mmol) in methanol (15 mL). The solution was stirred to obtain a clear solution to which pyridine (791.0 mg, 10 mmol) was added and further stirred. The reaction mixture was filtered and the filtrate was kept for crystallization at room temperature. Light pink X-ray quality single crystals of compound **1** were obtained after a week. M.p: 140–145°C. Yield: 195 mg (88%, based on dippH<sub>2</sub>). Anal. Calcd for C<sub>44</sub>H<sub>56</sub>CoN<sub>4</sub>O<sub>8</sub>P<sub>2</sub>: C, 59.39; H, 6.34; N, 6.30. Found: C, 59.01; H, 6.15; N, 6.37. FT-IR (KBr, cm<sup>-1</sup>): 3126(w), 3073(w), 2967(s), 2926(w), 2867(w), 2383(br), 1632(w), 1602(m), 1487(w), 1445(s), 1381(w), 1359(w), 1335(m), 1256(w), 1241(w), 1185(vs), 1166(v), 1143(w), 1109(s), 1094(m), 1069(m), 1040(m), 1007(w), 926(vs), 799(w), 765(m). TGA: Temp. range °C (% Weight loss): 30–410 (73.9); 420–800 (1.8).

**[Co(dipp)(bpy)(MeOH)<sub>2</sub>]<sub>2</sub>·2MeOH (2).** A solution of dippH<sub>2</sub> (129.0 mg, 0.5 mmol) in methanol (10 mL) was added to a solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (124.5 mg, 0.5 mmol) in methanol (15 mL) and stirred to get a clear solution. To the resulting solution solid 2,2'-bipyridine (78.0 mg, 0.5 mmol) was added and the solution turned brown. The reaction mixture was further stirred, filtered and the filtrate was kept for crystallization at room temperature. Brown X-ray quality crystals of compound **2** were obtained after two weeks. M.p: > 250°C. Yield: 157 mg (57 %, based on dippH<sub>2</sub>). Anal. Calcd for C<sub>50</sub>H<sub>74</sub>Co<sub>2</sub>N<sub>4</sub>O<sub>14</sub>P<sub>2</sub>: C, 52.91; H, 6.57; N, 4.94; Found: C, 52.84; H, 6.34; N, 5.25 ; FT-IR (KBr, cm<sup>-1</sup>): 3379(br), 2965(vs), 2929(vs), 2867(m), 1656(br), 1471(s), 1442(vs), 1339(m), 1257(m), 1181(vs), 1112(s), 1096(m), 1059(m), 948(vs), 766(s), 737(m). TGA: Temp. range °C (Weight loss, %): 30–105 (6.7); 105–485 (69.7); 485–1000(13.5).

**[Co(dipp)(phen)(MeOH)<sub>2</sub>]<sub>2</sub>·2MeOH (3).** Compound **3** was synthesized using 1,10-phenanthroline (140.1 mg, 0.5 mmol) instead of 2,2'-bipyridine in a similar manner as described above for compound **2**. Brown X-ray quality crystals of compound **3** were obtained after two days. M.p: >250°C. Yield: 160 mg (54 %, based on dippH<sub>2</sub>). Anal. Calcd for C<sub>54</sub>H<sub>74</sub>Co<sub>2</sub>N<sub>4</sub>O<sub>14</sub>P<sub>2</sub>: C, 54.82; H, 6.30; N, 4.74. Found: C, 54.71; H, 6.33; N, 4.89. FT-IR (KBr, cm<sup>-1</sup>): 3420(br), 3060(w), 2924(vs), 2854(m), 1624(m), 1514(w), 1451(m), 1425(m), 1257(w), 1083(vs), 1021(s), 984(vs), 900(m), 849(m), 766(m). TGA: Temp. range °C (Weight loss, %): 30–150 (9.4); 150–300(14.6); 300–1000(49.8).

**[Co(dipp)(imz)<sub>2</sub>]<sub>2</sub>·2MeOH (4).** A solution of dippH<sub>2</sub> (129.0 mg, 0.5 mmol) in methanol (10 mL) was added to a solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (124.5 mg, 0.5 mmol) in methanol (15 mL). The solution was stirred until it became clear and then solid imidazole (136.0 mg, 2.0 mmol) was added and the stirring was continued. The reaction mixture was filtered and the filtrate was kept at ambient temperature for crystallisation. Deep blue X-ray quality single crystals of compound **4** were isolated from the reaction mixture after three days. M.p: >250°C. Yield: 202 mg (74 %, based on dippH<sub>2</sub>). Anal. Calcd for C<sub>38</sub>H<sub>58</sub>Co<sub>2</sub>N<sub>8</sub>O<sub>10</sub>P<sub>2</sub>: C, 47.21; H, 6.05; N, 11.59. Found: C, 47.54; H, 5.78; N, 12.04. FT-IR (KBr, cm<sup>-1</sup>): 3455(br), 3135(w), 3024(w), 2964(m), 2930(m), 2870(w), 2846(w), 2704(w), 2630(w), 1617(w), 1543(w), 1505(w), 1468(m), 1446(m), 1384(w), 1327(m), 1257(m), 1185(vs), 1074(vs), 1051(s), 979(vs), 953(m), 917(s), 883(w), 818(m), 772(s), 760(m). TGA: Temp. range °C (% Weight loss): 30–520 (63.6); 520–1000 (5.4).

**[Co(dipp)(dmpz)<sub>2</sub>]<sub>2</sub>·2MeOH (5).** Compound **5** was synthesized following a similar procedure using 3,5-dimethylpyrazole (192.3 mg, 2.0 mmol) instead of imidazole described above for compound **4**. Deep blue X-ray quality single crystals of **5** were obtained from the reaction mixture after two weeks. M.p: >250 °C. Yield: 200 mg (76

%, based on  $\text{dippH}_2$ ). Anal. Calcd for  $\text{C}_{46}\text{H}_{74}\text{Co}_2\text{N}_8\text{O}_{10}\text{P}_2$ : C, 51.21; H, 6.91; N, 10.39; Found: C, 51.36; H, 6.73; N, 10.65; IR (KBr,  $\text{cm}^{-1}$ ): 3428(br), 3197(w), 3131(w), 3060(w), 2965(m), 2928(m), 2867(w), 1597(w), 1499(w), 1466(m), 1440(m), 1379(w), 1360(w), 1337(w), 1316(w), 1256(w), 1189(m), 1117(vs), 1052(s), 1000(vs), 904(m), 880(w), 770(m). TGA: Temp. range  $^{\circ}\text{C}$  (% Weight loss): 30-155 (3.1); 170-570 (67.6); 580-900 (1.5).

**[Co(dipp)(2-apy)]<sub>4</sub> (6)**. Compound **6** was synthesized using 2-aminopyridine (47.1 mg, 0.5 mmol) instead of 2,2'-bipyridine following a similar procedure described above for compound **2**. Deep blue rectangular X-ray quality crystals of compound **6** were isolated after three weeks. M.p.  $>250^{\circ}\text{C}$ . Yield: 165 mg (81 %, based on  $\text{dippH}_2$ ). Anal. Calcd for  $\text{C}_{68}\text{H}_{92}\text{Co}_4\text{N}_8\text{O}_{16}\text{P}_4$ : C, 49.89; H, 5.66; N, 6.84. Found: C, 49.56; H, 5.24; N, 6.97; FT-IR (KBr,  $\text{cm}^{-1}$ ): 3452(br), 2965(vs), 2867(vs), 2867(m), 1639(br), 1619(m), 1565(m), 1496(s), 1450(vs), 1337(m), 1257(m), 1170(vs), 1158(vs), 1047(m), 1017(vs), 922(s), 771(s). TGA: Temp. range  $^{\circ}\text{C}$  (Weight loss, %): 30-270 (1.7); 270-340 (36.8); 340-515(22.4); 515-1000(6.5).

**[Co<sub>4</sub>(dipp)<sub>4</sub>(2-apy)<sub>3</sub>(DMSO)]·(DMSO)·(H<sub>2</sub>O) (7)**. A solution of  $\text{dippH}_2$  (129.0 mg, 0.5 mmol) in methanol (10 mL) was added to a solution of  $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  (124.5 mg, 0.5 mmol) in methanol (25 mL). The solution was stirred until it became clear and then solid 2-aminopyridine (47.0 mg, 0.5 mmol) was added and the reaction mixture was stirred. The solvent was removed from the reaction mixture under reduced pressure and the blue residue obtained was redissolved in methanol (10 mL) and minimum amount of DMSO (2 mL) and kept at  $-15^{\circ}\text{C}$  for crystallization. Deep blue colour X-ray quality single crystals of compound **7** were isolated after three weeks. M.p.  $>275^{\circ}\text{C}$ . Yield: 195 mg (89 %, based on  $\text{dippH}_2$ ). Anal. Calcd for  $\text{C}_{67}\text{H}_{100}\text{Co}_4\text{N}_6\text{O}_{19}\text{P}_4\text{S}_2$ : C, 46.86; H, 5.87; N, 4.89; S, 3.73. Found: C, 47.28; H, 6.09; N, 5.33; S, 3.46. IR (KBr,  $\text{cm}^{-1}$ ): 3437(br),

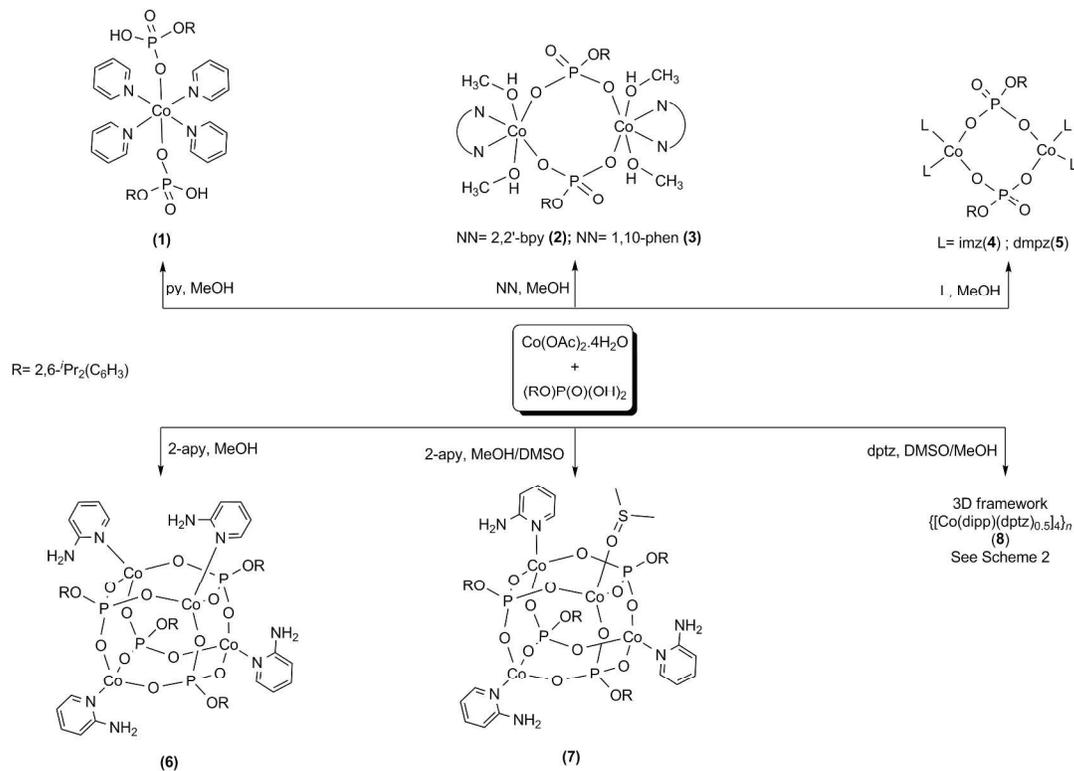
3215(w), 3065(w), 2964(m), 2867(w), 1635(s), 1567(m), 1497(s), 1450(m), 1338(w), 1257(w), 1171(vs), 1017(vs), 921(s), 771(s). TGA: Temp. range  $^{\circ}\text{C}$  (% Weight loss): 30-220 (3.3); 220-330 (28.7); 330-500 (29.9); 500-1000(4.8).

**{[Co(dipp)(dptz)<sub>0.5</sub>]<sub>4</sub>}\_n (8)**. This reaction has to be carried out in extremely dilute conditions in order to obtain crystalline product. In a typical experiment, a solution of  $\text{dippH}_2$  (12.9 mg, 0.10 mmol) and  $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  (12.5 mg, 0.1 mmol) in DMSO (100 mL) was taken in a 500 mL round bottomed flask and was layered with blank solvent methanol (100 mL) which in turn was layered by a methanol solution (100 mL) of dptz (11.8 mg, 0.05 mmol) and left undisturbed at room temperature. Deep blue-violet fine needles of **8** were obtained after one week. M.p.  $>250^{\circ}\text{C}$ . Yield: 14.5 mg (67 %, based on Co). Anal. Calcd for  $\text{C}_{72}\text{H}_{84}\text{Co}_4\text{N}_{12}\text{P}_4\text{O}_{16}$ : C, 49.90; H, 4.89; N, 9.70. Found: C, 47.36; H, 4.66; N, 7.79. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3434(br), 2965(m), 2923(m), 2868(s), 1618(br), 1467(m), 1440(m), 1393(m), 1256(m), 1165(vs), 1116(m), 1045(m), 1059(m), 1016(vs), 921(s), 774(s), 601(m). TGA: Temp. range  $^{\circ}\text{C}$  (% weight loss): 30-105(3.2); 105-175(6.1), 175-500(57.5), 500-1000(11.8).

## Results and discussion

### Synthetic Aspects

A successful attempt has been made in the present study to isolate cobalt organophosphates of different nuclearities in which the central cobalt ion is stabilized in different coordination numbers and environments, where factors such as cluster nuclearity, cobalt coordination number and the electronic environment around cobalt ions should greatly influence the magnetic behaviour. The modulation of nuclearity of the clusters can be controlled effectively by a proper choice of ancillary N-donor ligands (e.g. terminal N-donor versus chelating N,N-donor versus bridging N,N-donor ligands), while keeping the metal and phosphate source constant in all the reactions.



Scheme 1: Synthesis of cobalt organophosphates clusters and framework (1-8).

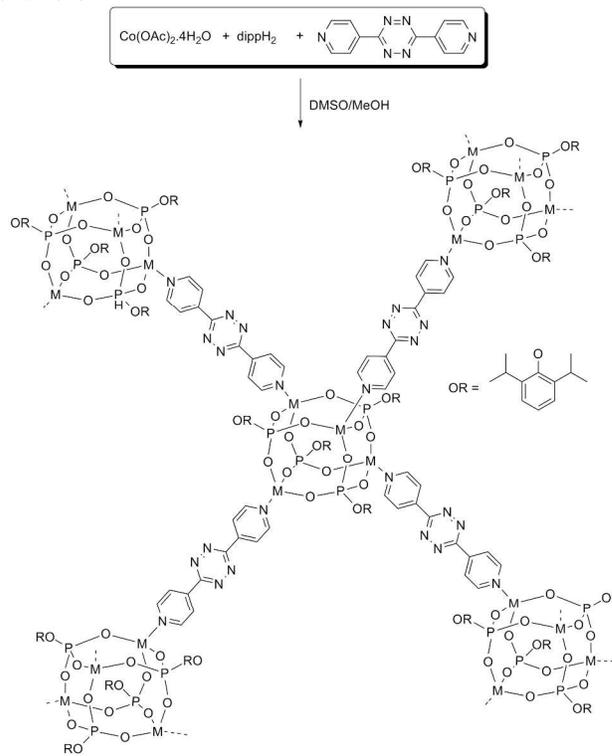
Schemes 1 and 2 summarize the variety of cobalt phosphates that have been isolated in the present study. The reaction of cobalt acetate tetrahydrate,  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  with  $\text{dippH}_2$  in an appropriate solvent in the presence of different N-donor ancillary ligands followed by slow crystallisation leads to the formation of different monomeric, dinuclear S4R, and tetranuclear D4R units in quantitative yields.

When excess of pyridine was used as the ancillary ligand in the reaction of cobalt acetate with  $\text{dippH}_2$  in methanol, analytically pure pink crystals of the mononuclear compound  $[\text{Co}(\text{dippH})_2(\text{py})_4]$  (**1**) were obtained in quantitative yield (Scheme 1). The compound possesses a single  $\text{Co}^{2+}$  ion in an octahedral environment with its equatorial positions occupied by the four pyridine ligands and the axial positions occupied by the phosphoryl oxygen atom from the two monoanionic phosphate ligands. The free P-OH group remains uncoordinated along with the dangling P=O moiety. The reaction of cobalt acetate tetrahydrate  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  with  $\text{dippH}_2$  in the presence of chelating ligands such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) in a 1:1:1 molar ratio, or unidentate ligands such as imidazole (imz) or 3,5-dimethylpyrazole (dmpz) in a 1:1:4 molar ratio, in methanol at ambient temperature yields analytically pure red crystals of dinuclear  $[\text{Co}(\text{dipp})(\text{bpy})(\text{MeOH})_2]_2 \cdot 2\text{MeOH}$  (**2**) and  $[\text{Co}(\text{dipp})(\text{phen})(\text{MeOH})_2]_2 \cdot 2\text{MeOH}$  (**3**), and deep blue crystals of  $[\text{Co}(\text{dipp})(\text{imz})_2]_2 \cdot 2\text{MeOH}$  (**4**) and  $[\text{Co}(\text{dipp})(\text{dmpz})_2]_2 \cdot 2\text{CH}_3\text{OH}$  (**5**), respectively. The  $\text{Co}_2\text{P}_2\text{O}_4$  core found in **2-5** resemble the single-4-ring (S4R) zeolite secondary building units (Scheme 1). In compounds **2** and **3**, the  $\text{Co}^{2+}$  ions are in an octahedral environment, with the equatorial plane occupied by the nitrogen atoms from the co-ligand and the oxygen atoms from the phosphoryl moieties, and the axial position occupied by the coordinated solvent molecules. The four coordination sites of the tetrahedral  $\text{Co}^{2+}$  ions in **4** and **5** are occupied by the two nitrogen atoms from the two co-ligands and the oxygen atoms of two different bridging phosphate moieties.

Direct reaction between  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{dippH}_2$  with 2-aminopyridine in a 1:1:1 molar ratio using methanol as the solvent at room temperature yields the symmetric tetranuclear cluster  $[\text{Co}(\text{dipp})(2\text{-apy})_4]$  (**6**) in quantitative yields. The compound is obtained as deep blue rectangular blocks having a core of  $\text{Co}_4\text{P}_4\text{O}_{12}$  that resembles the double-4-ring (D4R) zeolite SBU. All four of the  $\text{Co}^{2+}$  ions in the compound are in a tetrahedral environment. In the D4R cubane structure, the  $\text{Co}^{2+}$  ions are coordinated by three phosphoryl oxygen atoms from three different bridging phosphate ligands, but the remaining site is coordinated by the pyridyl nitrogen atom of the co-ligand. The direct reaction of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{dippH}_2$  and 2-aminopyridine in a 1:1:1 molar ratio using DMSO and methanol as the solvent at room temperature yields the asymmetric tetranuclear cluster  $[\text{Co}_4(\text{dipp})_4(2\text{-apy})_3(\text{DMSO})] \cdot (\text{DMSO}) \cdot (\text{H}_2\text{O})$  (**7**), which differs from **6** only by the presence of a mixture of both 2-apy and DMSO ligands on the cobalt centres (Scheme 1).

Formation of D4R cubanes with 2-apy as ancillary ligand suggested that 3-D frameworks can be built at ambient conditions if the N-donor used is not a mono-pyridine such as 2-apy, but a ditopic N,N'-donor such as 4,4'-bipyridine. The readily synthesizable ditopic linear N,N'-spacer 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (dptz) which has a longer N to N' distance (11.0 Å) has been used as the ancillary ligand in preference to 4,4'-bipyridine (7.0 Å). Combining cobalt acetate,  $\text{dippH}_2$  and dptz in methanol using a similar procedure to those used for preparation of **1-7** led to immediate precipitation of a blue-violet coloured product. Several attempts to crystallise this solid failed. The problem was then overcome by layering very dilute solutions of the reactants; a very dilute solution of  $\text{dippH}_2$  and  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  in DMSO was layered

with neat methanol which in turn was layered by a methanol solution of dptz. This method prevented immediate precipitation and led to the isolation of the cobalt phosphate 3D framework  $\{[\text{Co}(\text{dipp})(\text{dptz})_{0.5}]_4\}_n$  (**8**) (Scheme 2). This method exemplifies a soft approach for the synthesis of 3D frameworks at ambient conditions.



Scheme 2. Synthesis of 3-D framework  $\{[\text{Co}(\text{dipp})(\text{dptz})_{0.5}]_4\}_n$  (**8**).

### Infrared spectroscopy

The FTIR spectra of all the compounds (see supporting information, Figure S1) were measured as KBr diluted discs. The FTIR spectrum of compound **1** shows strong bands at 1166, 1109, and 926  $\text{cm}^{-1}$  which are assigned to the P=O, M-O-P asymmetric, and M-O-P symmetric stretching vibrations, respectively. In addition to these bands, a broad band at 2383  $\text{cm}^{-1}$  confirms the presence of a free P-OH group on the phosphate ligand. Compounds **2-8** similarly show the P=O, M-O-P asymmetric and M-O-P symmetric stretching vibrations in the region of 900-1200  $\text{cm}^{-1}$ . However, the infrared spectra of compound **2-8** are devoid of any absorption in the region of 2300  $\text{cm}^{-1}$ , indicating the complete neutralization (metallation) of the mono-organophosphate ester, leaving no free P-OH group.

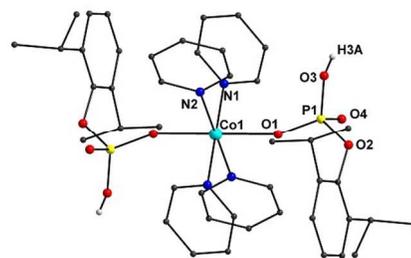
### Thermal decomposition studies

The thermal analysis of molecular cobalt phosphates leading to pure ceramic cobalt phosphates are of great interest. It has been shown by us some years ago that the di-tert-butylphosphate (dtbp) complexes of cobalt,  $[\text{Co}(\text{dtbp})_2]_n$ <sup>22a</sup> and  $[\text{Co}_4(\mu_4\text{-O})(\text{dtbp})_6]_n$ <sup>22d</sup> can act as single source precursors for the preparation of either pure  $\text{Co}(\text{PO}_3)_2$  or a mixture of  $\text{Co}_2\text{P}_2\text{O}_7/\text{Co}(\text{PO}_3)_2$  under very low temperatures (<200 °C). The metal to phosphate ligand ratio in all dtbp complexes is also maintained in the final ceramic phosphate and hence metal phosphate molecular complexes can be selectively used for the preparation of pure ortho-, meta- or pyrophosphates of any metal. Thermal analyses of all the new compounds hence were performed under a flow of dry nitrogen at a heating rate of 10 °C/min (See supporting information, Figure S2). Compound **1** melts

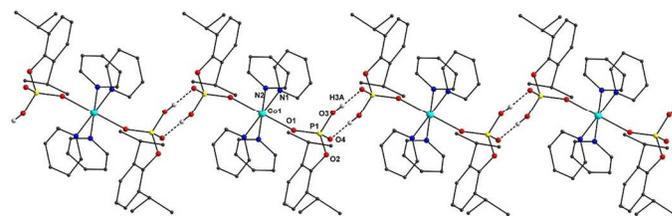
over a temperature range of 140–145 °C. The TGA trace of compound **1** show that the compound is stable only up to 100 °C, above which it shows decomposition up to 420 °C in three steps corresponding to the weight loss of the four pyridine molecules and the two aryl moieties of the phosphate ligand. From 420 °C to 800 °C there is a small weight loss of about 1.8 % corresponding to the loss of one water molecule, leaving behind a residue of 24.3 % corresponding to  $\text{Co}(\text{PO}_3)_2$  (theoretical value 24.4 %). Compound **2** on heating up to 230 °C exhibits a weight loss of 14.0 %, corresponding to the loss of six methanol molecules. Two 2,2'-bipyridine molecules and the aryl moieties on the phosphate ligands are lost on further heating until 650 °C, leaving  $\text{Co}_2\text{P}_2\text{O}_7$  as the residue. Structurally similar compound **3** shows similar thermal behaviour. Compound **4** is stable up to 250 °C, above which there is a sharp weight loss of 65.1% corresponding to the loss of the four imidazole molecules and the aryl part of the two phosphate ligands (theoretical loss 66.1%) leaving  $[\text{CoO}_3\text{P}(\text{OH})]$  which then eliminates water to form  $\text{Co}_2\text{P}_2\text{O}_7$  as the ceramic residue. In the case of compound **5**, the decomposition of ligands occurs in four steps up to 600 °C, corresponding to the loss of two methanol solvates, four coordinated 3,5-dimethylpyrazole molecules and the aryl part of the phosphate ligands, leaving  $[\text{CoO}_3\text{P}(\text{OH})]$ , which then eliminates water to leave 27.0 % of the initial mass at 1000 °C, corresponding to ceramic residue of  $\text{Co}_2\text{P}_2\text{O}_7$  (theoretical yield 27.0 %). Compound **6** is stable up to 400 °C after which it decomposes in three steps to form  $\text{Co}_2\text{P}_2\text{O}_7$ . Compound **7** exhibits a similar thermal behaviour to that of **6**. Framework **8** is stable up to 300 °C (excluding the initial loss of some adsorbed lattice molecules up to 200 °C). The aryl part of the phosphate ligand and the dptz linker are lost up to 500°C resulting in the exclusive formation of  $\text{Co}_2\text{P}_2\text{O}_7$ . In summary, apart from **1** (which yields  $\text{Co}(\text{PO}_3)_2$ ), all other molecular phosphates described in the present study show stepwise loss of various organics residues to finally yield the pyrophosphate  $\text{Co}_2\text{P}_2\text{O}_7$ .

#### Molecular structure of $[\text{Co}(\text{py})_4(\text{dippH})_2] (\mathbf{1})$

Rectangular pink crystals of **1** were obtained by slow evaporation of a methanol-pyridine mixture of cobalt acetate and dippH<sub>2</sub> ligand at room temperature after one week. Compound **1** crystallises in the centrosymmetric triclinic space group  $P\bar{1}$ . The final refined structure is shown in Figure 1. The central octahedral cobalt ion in **1** is surrounded by four pyridine ligands in the equatorial plane, with two phosphate moieties in the axial positions. The phosphate moieties coordinate to the metal centre in a unidentate fashion ([1.100] mode - Harris notation)<sup>36</sup> leaving free uncoordinated P=O and P–OH groups on each phosphate ligand. The P–O(M) distance is somewhat shorter than that of P–O(H) (P–O(Co) 1.497(1) Å, P–O(H) 1.567(1) Å). The average M–N distance is 2.181(1) Å, while the observed average M–O distance is 2.109(1) Å which is comparable with that reported for late transition metal phosphates.<sup>24</sup> The phosphoryl oxygen atoms are strongly involved in intermolecular interactions with the adjacent units to yield a zigzag 1-D polymeric structure (Figure 2) ( $\text{O}_3 \cdots \text{O}_4$  2.582(2) Å,  $\text{H}_3\text{A} \cdots \text{O}_4$  1.72(4) Å,  $\text{O}_3\text{--H}_3\text{A}$  0.87(4) Å,  $\text{O}_3\text{--H}_3\text{A} \cdots \text{O}_4$  174(3)°). It is worth noting that the structurally similar molecular metal phosphates  $[\text{M}(\text{dtpb})_2(\text{imz})_4]$  (M = Mn, Co, Ni, Cu, Zn) were reported by us.<sup>24,37</sup>



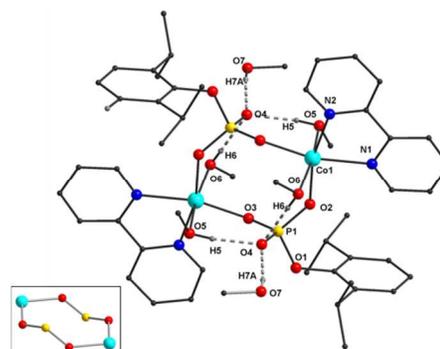
**Figure 1:** Molecular structure of **1** (all hydrogen atoms except for H3A are omitted for clarity).



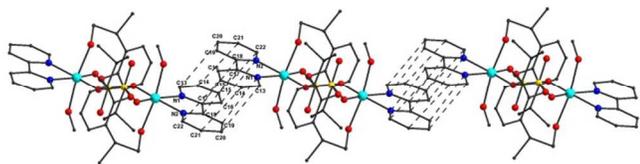
**Figure 2:** One-dimensional zig-zag polymeric structure through O–H $\cdots$ O hydrogen bonding interactions in **1** (all hydrogen atoms except for H3A are omitted for clarity).

#### Molecular structure of $[\text{Co}(\text{dipp})(\text{bpy})(\text{MeOH})_2] \cdot 2\text{MeOH} (\mathbf{2})$

Red hexagonal crystals of **2** were obtained after two weeks by slow evaporation of the reaction mixture at ambient conditions. The single crystal X-ray diffraction measurement for **2** indicates that the compound crystallises with one half of the molecule of cyclic cobalt phosphate and a lattice methanol in the asymmetric part of the unit cell (space group  $P2_1/n$ ) (Figure 3a). The octahedral cobalt is surrounded by a chelating 2,2'-bipyridine and two bridging phosphate oxygen atoms in the equatorial position and two coordinated methanol molecule in the axial positions. The bridging dipp ligand in **2** binds in a [2.110] mode.<sup>36</sup> Thus, two  $\text{Co}^{2+}$  ions and two phosphate anions form the single-four-ring (S4R) secondary building unit (SBU). The distance between two metal centres across the ring is 4.961 Å, while the corresponding P $\cdots$ P distance is 4.158 Å. The central eight-membered ring is involved in three hydrogen bonds (see ESI) that arise between the lattice and coordinated methanol molecule and the neighboring phosphoryl oxygen atoms, further stabilizing the coordinated methanol molecules. In addition, there is a strong  $\pi$ - $\pi$  stacking between the adjacent molecules involving the symmetry 2,2'-bipyridine rings (C18–C17' = 3.630 Å; C19–N1' = 3.660 Å; C20–C13' = 3.737 Å; C21–C14' = 3.757; C22–C15' = 3.713; N2–C16' = 3.647 Å) as shown in Figure 4.



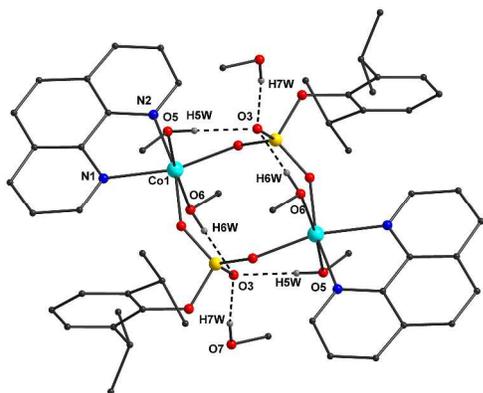
**Figure 3.** (a) Molecular structure of **2** (H-atoms are omitted for clarity). (Inset: core structure resembling a S4R unit).



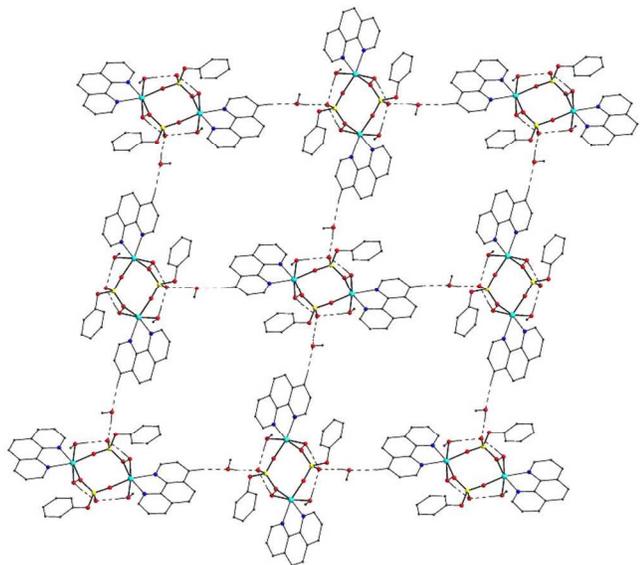
**Figure 4:** Slipped  $\pi$ - $\pi$  stacking between adjacent dinuclear complexes involving the symmetry related 2,2'-bipyridine rings in compound **2** (H-atoms are omitted for clarity).

#### Molecular structure of [Co(dipp)(phen)(MeOH)<sub>2</sub>]<sub>2</sub>·2MeOH (**3**)

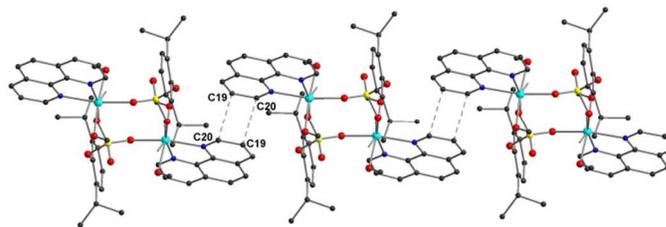
Red crystals for **3** were grown by the slow evaporation of solvent from the reaction mixture at ambient temperature. Compound **3** crystallises in the monoclinic space group  $P2_1/n$  with one half of the molecule of cyclic cobalt phosphate and one lattice methanol in the asymmetric unit. The structure of **3** is isostructural to that of **2**, with the main difference being the replacement of the chelating ligand 2,2'-bipyridine by 1,10-phenanthroline (Figure 5). The central Co<sub>2</sub>P<sub>2</sub>O<sub>4</sub> eight-membered ring is enveloped by intramolecular hydrogen bonds (O5–H5W...O3 2.696(2) Å = 171.1(1)°; O6–H6W...O3 2.730(2) Å, =169.9(1)°) that arise between coordinated methanol O–H groups and the phosphoryl oxygen atoms and thus, a twelve-membered, an eight-membered, and four six-membered rings are formed in the dimeric unit.



**Figure 5:** Molecular structure of **3** (lattice methanol and hydrogen atoms except H6W and H5W are omitted).



**Figure 6:** Rectangular grid formation in **3** through intermolecular H-bond interactions (H-atoms and isopropyl group have been omitted for clarity).

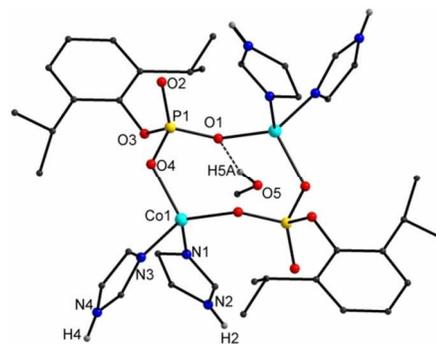


**Figure 7:** The  $\pi$ - $\pi$  stacking between the symmetrically related 1,10-phenanthroline units of adjacent dimers of **3** (H-atoms have been omitted for clarity).

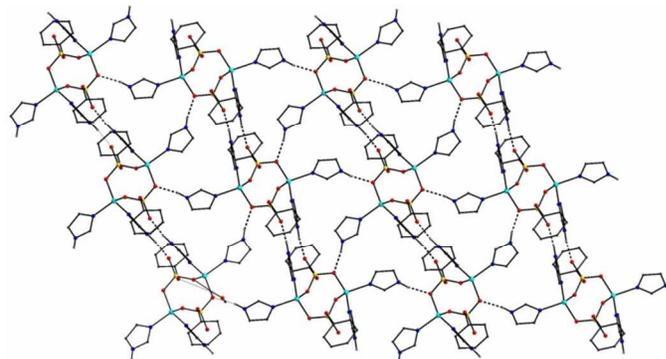
In addition, the lattice methanol molecules and the aromatic C–H groups bridge the cobalt phosphate dimers by intermolecular hydrogen bonds (C15–H15...O7 = 3.262(3) Å, 149.6(2)°; O7–H7W...O3 = 2.721(3) Å, 172.7(2)°) and result in the formation of an infinite two-dimensional grid-like structure (Figure 6). Similar to compound **2**, there is additional slipped  $\pi$ - $\pi$  stacking among the adjacent molecules involving the symmetry related 1,10-phenanthroline rings (C19–C20' = 3.375 Å) (Figure 7).

#### Molecular structure of [Co(dipp)(Imz)<sub>2</sub>]<sub>2</sub>·2MeOH (**4**)

Deep blue crystals of **4** were isolated after three days of slow evaporation of the solvent from the reaction mixture at ambient temperature. Compound **4** crystallizes in the centrosymmetric orthorhombic space group  $Pbca$  with half of the molecule in the asymmetric unit. A perspective view of the final refined molecular structure is shown in Figure 8. The cobalt(II) ions and phosphorus atoms exhibit a distorted tetrahedral geometry. The observed Co–O and Co–N distances are Co1–O1...1.936(3), Co1–O4...1.946(3), Co1–N1...2.009(3) and Co1–N3...2.009(3) Å, respectively. The cobalt and phosphorus atoms are coplanar in the eight-membered rings. The two Co–O–P angles are 122.07(2)° and 135.10(2)°.



**Figure 8:** Molecular structure of **4** (Selected hydrogen atoms have been omitted for the sake of clarity).

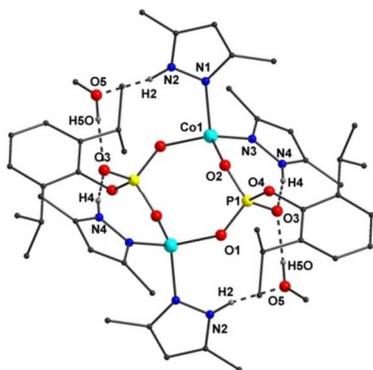


**Figure 9:** Rectangular grid formation through intermolecular N–H...O hydrogen bonding interactions of compound **4**.

The average length of the face diagonal in the Co...Co direction is 3.943 Å and the corresponding P...P distance is 4.852 Å. The lattice hydroxyl group of the methanol molecule is hydrogen bonded to the phosphoryl oxygen (O5-H5A...O1 = 2.826(5) Å, 158.0°). The source of intramolecular hydrogen bonding interactions in this molecule is N-H donor and phosphoryl oxygen acceptor. There are two such intermolecular N-H...O hydrogen bonding interactions in this molecule (N2-H2...O2' = 2.689(4) Å, 153.8°; N4-H4...O4'' = 2.810(5) Å, 170(7)°, which leads to the formation of a 2D rectangular grid as shown in Figure 9.

#### Molecular structure of [Co(dmpz)<sub>2</sub>(dipp)]<sub>2</sub>·2MeOH (5)

Deep blue crystals of **5** were grown from the reaction mixture by slow evaporation of the solvent at room temperature. Compound **5** crystallizes in the triclinic space group *P* $\bar{1}$ . The core structure of the molecule is similar to compound **4**. The four-coordinate tetrahedral cobalt is surrounded by two 3,5-dimethylpyrazole ligands and two oxygen atoms of two different bridging phosphate ligands. The average angle around cobalt is 109.37° (range 103.20 - 116.49°). The distance between the diagonally opposite cobalt ions is 4.307 Å. The phosphoryl oxygen atom O3 participates in intramolecular H-bonding with the N-H protons of the pyrazole ring (N4-H4...O3#1 = 2.696(2) Å, 170(2)°) and with the lattice methanol molecule (O5-H5A...O3 = 2.6500(19) Å, 176(3)°) as shown in Figure 10. The -OH of lattice methanol is also involved in H-bonding with the imidazole -NH proton (N2-H2...O5 = 2.778(2) Å, 162(2)°). The presence of two methyl groups on pyrazole precludes formation of any intermolecular hydrogen bonds.



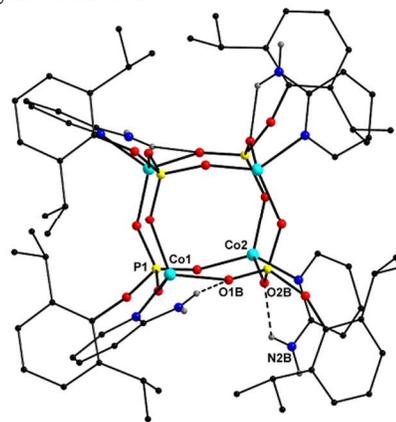
**Figure 10.** Molecular structure of **5** showing intramolecular H-bonding interactions (Selected H-atoms have been omitted for clarity).

#### Molecular structure of [Co(dipp)(2-apy)]<sub>4</sub> (6)

Air stable deep blue single crystals of **6** were obtained directly from a methanol solution of the polycrystalline sample after three weeks. Compound **6** crystallises in the centrosymmetric monoclinic space group *C*2/*c* with one half of the molecule occupying the asymmetric unit (Figure 11). The molecule is composed of four cobalt atoms, four phosphate ligands, and four 2-aminopyridine ligands arranged in the form of a closed cluster. In the Co<sub>4</sub>O<sub>12</sub>P<sub>4</sub> central core of this tetrameric cobalt phosphate cluster, cobalt and phosphorus atoms occupy alternate vertices of a cubane (Figure 12), similar to a number of metal phosphonates with a M<sub>4</sub>O<sub>12</sub>P<sub>4</sub> core,<sup>17,18b-c</sup> and metasiloxanes<sup>16a-d</sup> with a M<sub>4</sub>O<sub>12</sub>Si<sub>4</sub> core. Compounds with this core have assumed particular importance due to their resemblance to the commonly observed D4R (double-four-ring) SBU of zeolites and other framework solids. Although first row divalent transition metal ions such as Zn<sup>2+</sup>, Mn<sup>2+</sup>, and Cu<sup>2+</sup> have already been incorporated inside clusters analogous to compound **6**, this is the first example of a D4R cobalt phosphate.<sup>24</sup> Each of the

Co...P edges of the cube is bridged by a phosphate oxygen in a  $\mu^2$  fashion, resulting in the formation of six non-planar Co<sub>2</sub>O<sub>4</sub>P<sub>2</sub> eight membered rings that adopt a distorted pseudo-C<sub>4</sub> crown conformation. The bridging dipp ligand in **6** binds in a [3.111] mode.<sup>36</sup> The average P-O bond distance within the cage is 1.538 Å. The average Co-N and Co-O distances are 2.0393 Å and 1.9309 Å, respectively. All the cobalt and phosphorus centres maintain near ideal tetrahedral coordination geometry.

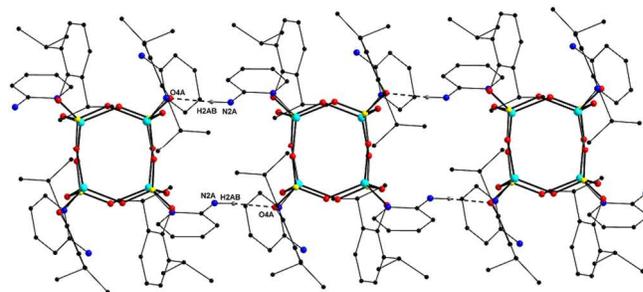
The presence of an amino substituent on the pyridine ring leads to an interesting polymeric chain formation. While each of the four -NH<sub>2</sub> groups in compound **6** forms an intramolecular N-H...O interaction with one of the framework oxygens, two -NH<sub>2</sub> groups are also involved in intermolecular N-H...O interactions with the adjacent molecules that result in the formation of a 1D assembly as shown in Figure 13. There are two unique intramolecular hydrogen bonds in compound **6** through the interaction of amino hydrogen bonds with the cubane framework oxygen atoms (N2A-H2AA...O1B = 2.988(3) Å, 154.3° and N2B-H2BA...O2B = 2.939(3) Å, 135.5°). The intermolecular hydrogen bond (N2A-H2AB...O4A = 3.009(2), 155.6°) is the source of self-assembly, in this case leading to a railroad like polymer formation.



**Figure 11:** Molecular structure of **6** (selected hydrogen atoms are omitted for clarity).



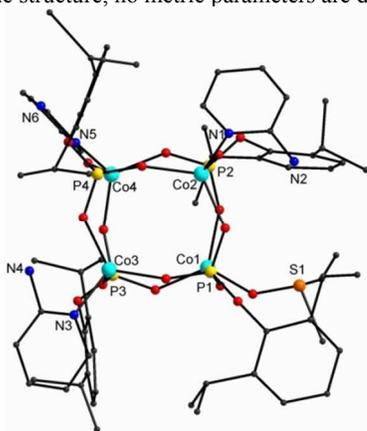
**Figure 12:** Core structure of **6** resembling a D4R cubane structure.



**Figure 13:** Intermolecular hydrogen bonding linkage for compound **6**. (Selected hydrogen atoms omitted for clarity).

### Molecular structure of $[\text{Co}_4(\text{dipp})_4(2\text{-apy})_3(\text{DMSO})] \cdot (\text{DMSO}) \cdot (\text{H}_2\text{O})$ (**7**)

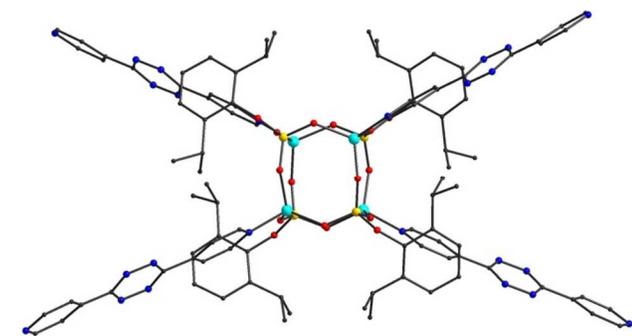
In spite of our repeated efforts to grow X-ray quality crystals of **7**, only weakly diffracting crystals were obtained presumably due to the asymmetric tetrameric cluster. Using one of the best available crystals, the molecular structure of **7** could be solved and refined to a reasonable convergence. Compound **7** crystallises in the triclinic space group  $P\bar{1}$  with a complete molecule in the asymmetric unit (Figure 14). The molecule is composed of four cobalt atoms, four phosphate ligands, three 2-aminopyridine ligands, one coordinated DMSO molecule, and with one DMSO and one water molecule in the lattice. The molecules adopt the same cubane structure seen for compound **6**, with the cobalt and phosphorus atoms occupying the alternate vertices. Compound **7** represents the first example of an asymmetric cubane where one of the four cobalt centres is coordinated by a DMSO ligand while the other three are coordinated by 2-apy ligand. Due to the poor resolution of the structure, no metric parameters are discussed.



**Figure 14:** Molecular structure of **7** (lattice solvent molecules and H-atoms are omitted for clarity).

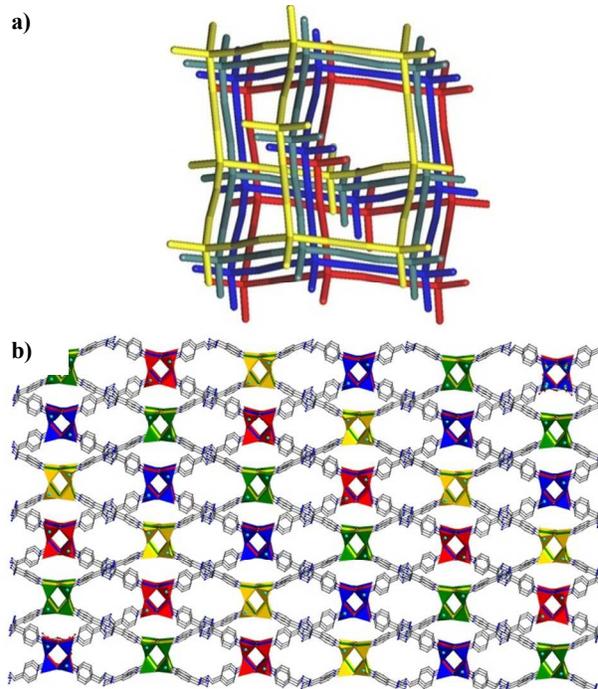
### Molecular structure of $[\text{Co}(\text{dipp})(\text{dptz})]_n$ (**8**)

X-ray quality crystals of framework **8**, grown by a diffusion method using very dilute solutions of the reactants, crystallise in the tetragonal space group  $P4/mnc$ . The asymmetric unit of the crystal consists of one cobalt ion, one phosphate ligand and half of the dptz linker molecule. The D4R SBU acts as tetrahedral-4-connected nodes which are then linked with the other SBU through dptz ligand with coordinate linkages (Figure 15). The length of the linker dptz molecule is 11.055(1) Å whereas the distance between two cobalt ions of two different SBU through the linker is 15.092(2) Å.



**Figure 15:** Molecular structure of compound **8** (Hydrogen atoms are omitted for clarity).

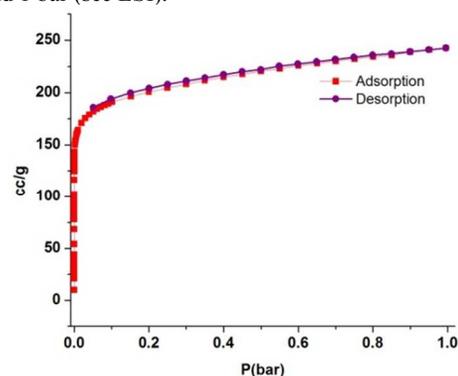
The linking of the D4R SBU with the linear linker leads to a robust three dimensional framework with hexagonal channels (Figure S5) and a diamond network, as expected from interconnected tetrahedral nodes (Figure S6). Topological analysis of the three dimensional network using TOPOS program showed a fourfold interpenetrated network with 4c-uninodal structure with the point symbol  $6^6$  (Figure 16).<sup>38</sup>



**Figure 16:** Net and polyhedral view four-fold interpenetrated framework in **8**.

### Gas Adsorption Studies

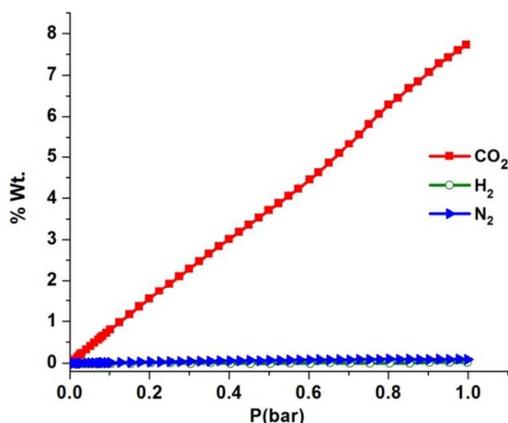
Crystals of compound **8** were separated from the mother liquor and washed several times with methanol followed by repeated solvent exchange with  $\text{CH}_2\text{Cl}_2$  for 48h. The sample was then activated at 120 °C under vacuum. Powder X-ray diffraction pattern of the activated sample is similar to the simulated single X-ray diffraction pattern (Figure S4).  $\text{N}_2$  physisorption measurements were performed at 77 K upto 1 bar. The BET surface area of the framework was found to be 605  $\text{m}^2/\text{g}$  and the Langmuir surface area to be 1024  $\text{m}^2/\text{g}$  (Figure 17). The  $\text{N}_2$  adsorption curve shows a type-I profile which is indicative of the microporous or nanoporous nature of the framework. The framework shows 0.84 wt% adsorption of  $\text{H}_2$  at 77K and 1 bar (see ESI).



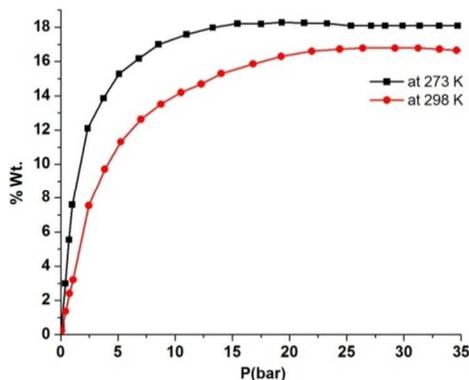
**Figure 17:**  $\text{N}_2$  adsorption isotherm at 77K for framework **8**.

Metal organic frameworks containing nitrogen rich surfaces have been shown to be better scavengers of CO<sub>2</sub> compared to the N-free surfaces.<sup>7,39</sup> As the framework material **8** contains bridging ligand dptz with N-atoms, CO<sub>2</sub> adsorption studies were carried out at 273K. The framework material **8** shows a type-II adsorption isotherm for CO<sub>2</sub> (Figure 18) in the lower pressure region up to 1 bar with uptake capacity of 7.80 wt. %. The framework does not adsorb N<sub>2</sub> or H<sub>2</sub> at this temperature indicating the highly selective nature of the framework towards CO<sub>2</sub>. High pressure gas adsorption isotherms (Figure 19) carried out at 273K and 278 K shows that the adsorption by the framework saturates at around 15 bar with CO<sub>2</sub> uptake capacities of 18.0 and 15.5 wt. % respectively although higher CO<sub>2</sub> uptake has been previously reported for other MOFs.<sup>7a</sup>

The volume of the unit cell of framework compound **8** is 10057 Å<sup>3</sup> and the framework has a void space of 1285 Å<sup>3</sup> per unit cell. This void can contain 22.05 wt % of CO<sub>2</sub> at 273K, which is slightly higher than the experimental value of 18 wt %. As the adsorbed CO<sub>2</sub> gas cannot be assumed to occupy the whole void space available, the numbers obtained for the maximum uptake of CO<sub>2</sub> at varying pressures are reasonable.



**Figure 18.** CO<sub>2</sub> along with N<sub>2</sub> and H<sub>2</sub> adsorption in the framework of framework **8** at 273 K, showing high selectivity for CO<sub>2</sub>.

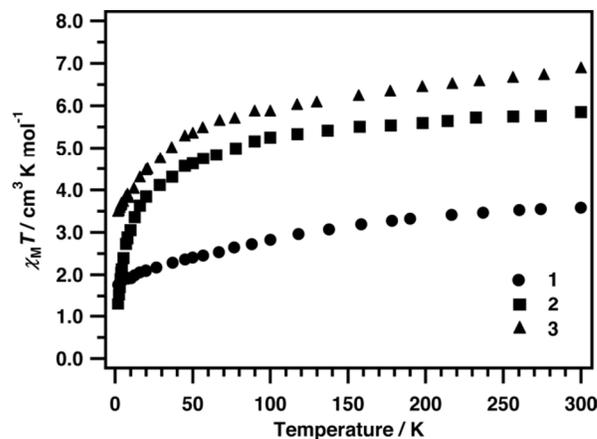


**Figure 19.** High pressure CO<sub>2</sub> adsorption isotherm at 273K and 298 K for framework **8**.

### Magnetic properties of compounds 1-3

Temperature-dependent magnetic susceptibility and field-dependent magnetisation measurements were carried out on all the new compounds. Complex **1** contains a single Co<sup>2+</sup>, 3d<sup>7</sup> ion in a pseudo-octahedral environment, and hence has a <sup>4</sup>T ground term with unquenched orbital angular momentum. This is consistent with its room temperature  $\chi T$  value of ca. 3.5 cm<sup>3</sup> K mol<sup>-1</sup> (where  $\chi$  is the

molar magnetic susceptibility), which decreases with decreasing temperature (Figure 20). The low temperature limiting value of  $\chi T$  (ca. 1.8 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K) and the saturation of the molar magnetisation ( $M$ ) at 2 K (2.2  $\mu_B$  above ca. 3 T, Figure S10) are consistent with thermal depopulation to a ground Kramers doublet with  $g_{\text{eff}} = 4.4$ , typical for six-coordinate Co<sup>2+</sup>.

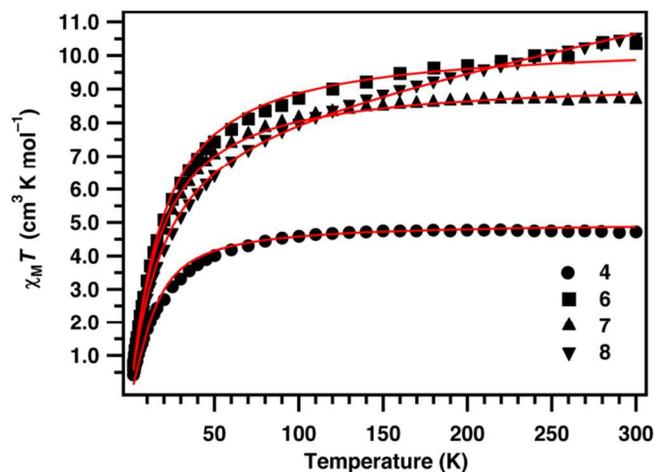


**Figure 20:** Temperature-dependent magnetic susceptibility of compounds 1–3 measured under a static magnetic field ( $H$ ) of 0.1 T.

Although compounds **2** and **3** both comprise two six-coordinate Co<sup>2+</sup> ions bridged by two phosphates, their low temperature magnetic behaviours are markedly different. For **3**, both  $\chi T(T)$  and  $M(H)$  are similar to the sum of two independent six-coordinate Co<sup>2+</sup> ions ( $\chi T = 3.46$  cm<sup>3</sup> K mol<sup>-1</sup> at 2 K;  $M(H)$  saturating at ca. 4.89  $\mu_B$  above  $H = 4$  T at 2 K, Figure S11) indicating no or very weak intramolecular exchange. In contrast,  $\chi T(T)$  for **2** undergoes a sharper downturn below ca. 20 K, reaching 1.30 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K, and  $M(H)$  at 2 K rises more slowly and fails to saturate up to 7 T (Figure S12). Both of these factors indicate a weak antiferromagnetic interaction in **2**. Hence, in both cases the exchange is very weak: given the orbitally degenerate nature of the paramagnetic ions, we have not attempted to model these data. However, we note that even small changes to weak exchange interactions can lead to significant changes to the observed magnetic behaviour: such changes have been seen in six-coordinate Co<sup>2+</sup> dimers (even antiferro- to ferro-magnetic) on substitution of terminal ligands with no change to the bridging arrangement.<sup>40</sup>

In contrast to **1–3**, complexes **4–8** contain pseudo-tetrahedral Co<sup>2+</sup> ions (<sup>4</sup>A ground term), hence their magnetic properties are in principle amenable to treatment with a spin-only Hamiltonian. For the dimetallics **4** and **5**,  $\chi T$  is ca. 4.5 cm<sup>3</sup> K mol<sup>-1</sup> at room temperature, consistent with the sum of two  $S = 3/2$  ions with  $g > 2.2$ , which decreases with decreasing temperature (Figure 24). For compound **4**,  $\chi T(T)$  decreases more rapidly below ca. 10 K, tending towards nil (reaching 0.43 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K). This is consistent with antiferromagnetic coupling between the Co<sup>2+</sup> ions, as is the low temperature magnetisation behaviour, rising only slowly (and almost linearly) with increasing field and failing to saturate (Figure S13). The data for **5** are near identical at higher temperatures, as expected, but are complicated by a sudden (field-dependent) rise of  $\chi T$  below 5 K (Figure S16), accompanied by a rapid magnetisation onset at low field in  $M(H)$  at 1.8 K (Figure S17). We do not know the origin of this effect: although it is possible that there is a long-range ordering/canting effect at low temperature, there is no direct evidence for this and no more obvious intermolecular pathways in **5** than in **4**. The most likely explanation is a magnetic impurity (Figure S18). The magnetic behaviour of the

Co<sub>4</sub> cubane clusters **6** and **7**, and of the D4R SBU-based framework material **8**, are analogous to that of **4** (Figure 21): in each case  $\chi T$  at room temperature is reasonable for the sum of four  $S = 3/2$ , but with some variation in  $g$ , and  $\chi T(T)$  decreases on cooling, tending towards nil at base temperatures. In each case,  $M(H)$  rises only slowly with  $H$  (Figures S14, S15, S19).



**Figure 21:** Temperature-dependent magnetic susceptibilities of compounds **4**, **6**, **7** and **8** measured under a static field of 0.1 T (**6**) and 0.5 T (**4**, **7** and **8**). Red lines are best fits with spin Hamiltonian (1) and the parameters in the main text.

We have attempted to model these data to the simplest possible spin Hamiltonian (1):

$$H = \sum_i g \mu_B \hat{S}_i \cdot \mathbf{H} - 2J_{ij} \sum_{i,j;i \neq j} \hat{S}_i \cdot \hat{S}_j \quad (1)$$

i.e. with an isotropic  $g$ -value for each  $S = 3/2$  centre, and a single unique and isotropic exchange interaction  $J$  (sum over one interaction in **4**; sum over six interactions in **6** and **7** where the metal ions lie on the vertices of a tetrahedron). Best fits to  $\chi T(T)$ , allowing  $g$  and  $J$  to vary as free parameters, gave:  $g = 2.31$ ,  $J = -2.4 \text{ cm}^{-1}$  (**4**);  $g = 2.36$ ,  $J = -1.5 \text{ cm}^{-1}$  (**6**);  $g = 2.23$ ,  $J = -1.4 \text{ cm}^{-1}$  (**7**);  $g = 2.07$ ,  $J = -1.46 \text{ cm}^{-1}$  (**8**) (Figure 21). These parameters also reproduce the slowly increasing  $M(H)$  behaviour (e.g. Figures S14 and S15), although not the details of the very shallow curvature in each case. This implies that Hamiltonian (1) is not sufficient for the  $M(H)$  data. The most obvious omission is the single ion zero-field splittings, which can be very large for pseudo-tetrahedral Co<sup>2+</sup> ions.<sup>41</sup> We have not attempted to include this given the number of free variables necessary to produce reasonable fits (e.g.  $g$ -anisotropy, axial and rhombic ZFS terms). [Note also that attempts to model the data including only ZFS terms (i.e. nil exchange) were unsuccessful.] Nevertheless, the magnetic data are clear in revealing a weak but significant antiferromagnetic exchange interaction between neighbouring ions in **4-8**. The similarity of  $J$  between the di- and tetra-metallics is expected because in both sets of complexes each pair of Co<sup>2+</sup> ions is bridged solely by two 1,3-phosphates. Finally, we note that some tetranuclear Co(II) carboxylate clusters are known to exhibit single molecule magnet properties,<sup>26</sup> however, these examples are six-coordinate at Co and hence are not directly comparable to **6-8**.

## Conclusions

We have synthesized a series of cobalt phosphates from the organic soluble 2,6-di-*iso*-propylphenylphosphate ligand and different ancillary ligands and all the reactions were carried out at ambient temperature and atmospheric pressure in different organic solvent. All the compounds were characterized by different

spectroscopic and single crystal X-ray diffraction studies. Compounds **6** and **7** represent the first examples of stabilized tetrahedral cobalt ions in a phosphate cluster possessing D4R core geometry. Use of the linear N-donor ditopic linker 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (dptz) as an ancillary ligand at ambient conditions (no hydrothermal or high temperature reaction) leads to the formation of a robust three dimensional four-fold interpenetrated network based on the D4R platform,  $\{[\text{Co}(\text{dipp})(\text{dptz})_{0.5}]_4\}_n$  (**8**). The cobalt organophosphate framework **8** shows highly selective CO<sub>2</sub> adsorption over N<sub>2</sub> and H<sub>2</sub>. The CO<sub>2</sub> adsorption reaches a maximum of 18 weight percentage at 15 bar (20 °C), which is a significant value considering the fact that this is the first example of a metal organophosphate framework being utilized for CO<sub>2</sub> adsorption. These values can be improved in future by preparing lighter phosphate frameworks containing small phosphate esters and lighter metal ions. The magnetic interactions between the cobalt ions via the bridging phosphonate moiety were found to be weak and antiferromagnetic. The fact that porous frameworks based on D4R SBU can be synthesised using soft chemical methods provides ample opportunity to tune the pores of the 3D framework by proper choice of the ditopic ligands with varying length and different functionalities.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Spectral data for compounds **1-8** and additional crystal structure details including CIF. CCDC for **1-3** (1024703-1024705), **4** (1030578), **5-6** (1024707-1024708) and **8** (1024709). See DOI: 10.1039/b000000x/

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## Discrete and polymeric cobalt organophosphates: Isolation of a 3-D cobalt phosphate framework exhibiting selective CO<sub>2</sub> capture

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Auxiliary ligand assisted structural diversity has been achieved in the case of cobalt organophosphates. Use of rigid ditopic linear linker leads to the formation of a four-fold interpenetrated 3D framework based on zeo-type D4R platform showing selective CO<sub>2</sub> capture over N<sub>2</sub> and H<sub>2</sub>.

