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Discrete and polymeric cobalt organophosphates: Isolation of a 3-D cobalt phosphate framework exhibiting selective CO₂ 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-propylphenylphosphinate (dippH₄) in methanol or DMSO in the presence of ancillary N-donor ligands, leads to the formation of mononuclear octahedral cobalt phosphate [Co(dippH₄)(py)₆] (1), dinuclear octahedral [Co(dipp)(NN)(MeOH)₂]·2MeOH (NN = bpy 2; phen 3), tetrahedral cobalt phosphates [Co(dipp)(L)₂]·2(MeOH) (L = imz 4; dmpz 5) and symmetric and asymmetric tetranuclear tetrahedral cobalt phosphates [Co(dipp)(2-apy)₇̅] (6) and [Co₄(dipp)(2-epy)₉]{DMSO}]·(H₂O) (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)_3]_4} (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 Co₃P₃O₁₂ ring, resembles the S4R (single-4-ring) SBU of zeolites, whereas the Co₄P₄O₁₂ inorganic core found in compounds 6 and 7, resembles the D4R (double-4-ring) SBU. Cobalt organophosphate framework 8 shows significant CO₂ adsorption at 273 K (7.73 wt % at 1 bar and 18.21 wt % at 15.5 bar) with high selectivity to CO₂ uptake over N₂ and H₂ 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 CO₂ generated from industrial and energy-related sources is one of the major challenges that the scientific community is trying to address in recent times. As per the data of the Intergovernmental Panel on Climate Change, the major contributor to the increase in concentration of anthropogenic greenhouse gas is CO₂ released from the burning of fossil fuels. Further, the Energy Information Administration (EIA) projects that the world’s energy consumption will shoot up by 56% between 2010 and 2040. Various methods have been used to adsorb and sequester CO₂, such as by the use of amines or by adsorption through materials such as activated carbons and zeolites. Recently, metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) 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 CO₂ adsorption due to the enhanced dipole-quadrupole interactions present in such systems. Although a large number of MOFs have been synthesised from various ligands with the goal of improved CO₂ 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 AlPOs) by Flanigen et al. in 1982 inspired exploration of other types of zeolite-like phosphate materials. Metallophosphonate layered solids have also been extensively investigated during this period not only because of their structural diversity, but also because of their potential applications in the fields of absorption and separation, catalysis, photoluminescence, and proton conductivity.

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 aluminophosphates, and phosphonic acids. Due to the presence of two acidic protons and one phosphoryl oxygen, both phosphate esters (RO)P(O)(OH)₃ and phosphonic acids RP(O)(OH)₂ tend to embrace more metal ions around them to form larger aggregates. A large number of discrete molecular metallophosphonates and metallophosphates have been synthesised in recent years starting from phosphonic acids and phosphate esters. Much of the recent thrust in metallophosphonate discrete clusters can be attributed their ability to...
exhibit interesting magnetic properties, including magnetocaloric effects. 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. Further, cobalt based phosphate systems have a tendency to act as catalysts particularly for the oxidation of water. Although a large number of discrete clusters, as well as layered, pillared, and open framework structures of cobalt organophosphonates are reported in the literature, those of cobalt organophosphates are relatively rare.

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 to cobalt based systems, and here we report on the auxiliary ligand assisted structural diversity of cobalt organophosphates based on a phosphate monoester, diphenylphosphine oxide (dippO).

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 discs. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. 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 analyzer. 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. Single crystal X-ray diffraction data were collected either on an Oxford Xcalibur CCD diffractometer or a Rigaku Saturn724+ diffractometer using MoKα radiation.

Syntheses

All the compounds prepared in this study are air and moisture stable. Therefore all manipulations were carried out under nitrogen or argon gas to avoid contamination with oxygen.

Co(dipp)(bpy)(MeOH)OCl (1). A solution of dipH2 (129.0 mg, 0.5 mmol) in methanol (10 mL) was added to a solution of Co(OAc)2⋅4H2O (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 dipH2). Anal. Calcld for C46H42CoN4O8P: C, 59.39; H, 6.57; N, 6.30. Found: C, 59.21; H, 6.15; N, 6.37. FT-IR (KBr, cm⁻¹): 3126(w), 3073(w), 2976(s), 2920(w), 2867(w), 2838(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), 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)2OCl2 (2). A solution of dipH2 (129.0 mg, 0.5 mmol) in methanol (10 mL) was added to a solution of Co(OAc)2⋅4H2O (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 pink. X-ray quality single crystals of compound 2 were obtained after two days. M.p: >250°C. Yield: 157 mg (57 %, based on dipH2). Anal. Calcld for C56H46CoN4O8P: C, 59.01; H, 6.15; N, 6.30. Found: C, 58.91; H, 6.25; N, 6.49. FT-IR (KBr, cm⁻¹): 3126(w), 3073(w), 2976(s), 2920(w), 2867(m), 2838(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), 1094(m), 1069(m), 1040(m), 1007(w), 926(vs), 799(w), 765(m). TGA: Temp. range °C (% Weight loss): 30-105 (6.7); 105-485 (69.7); 485-1000(13.5).

Co(dipp)(phen)(MeOH)2OCl (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 dipH2). Anal. Calcld for C54H40CoN4O8P: C, 54.82; H, 6.30; N, 4.74. Found: C, 54.82; H, 6.33; N, 4.89. FT-IR (KBr, cm⁻¹): 3420(br), 3060(w), 2924(w), 2854(m), 1624(m), 1514(w), 1451(s), 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)2OCl2 (4). A solution of dipH2 (129.0 mg, 0.5 mmol) in methanol (10 mL) was added to a solution of Co(OAc)2⋅4H2O (124.5 mg, 0.5 mmol) in methanol (15 mL). The solution was stirred until it became clear and then solid imidazole (132.5 mg, 2.0 mmol) was added and the stirring was continued. The reaction mixture was filtered and the filtrate was kept for crystallization at room temperature. 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 dipH2). Anal. Calcld for C46H40CoN4O6P: C, 57.42; H, 6.05; N, 11.59. Found: C, 57.42; H, 5.78; N, 12.04. FT-IR (KBr, cm⁻¹): 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)2OCl2 (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
Deep blue rectangular X-ray quality crystals of compound following a similar procedure described above for compound dippH solution of Co(OAc)\textsubscript{2} isolated after three weeks. M.p: >250 °C.

**IR (KBr, cm\textsuperscript{-1}):**
- 3437(br), 3360(w), 3300(m), 3199(w), 3147(w), 3060(m), 2965(m), 2928(m), 2867(w), 1597(w), 1499(m), 1466(m), 1440(m), 1379(w), 1360(w), 1357(w), 1316(w), 1256(w), 1117(vs), 1052(s), 1000(vs), 904(m), 880(w), 770(m).

**TGA: Temp. range °C (% Weight loss):**
- 30-155 (3.1); 170-570 (67.6); 580-900 (1.5).

**[Co(dipp)(2-apy)]\textsubscript{2} (6).** Compound 6 was synthesized using 2-aminoypyridine (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 °C. Yield: 165 mg (81 %, based on dippH). Anal. Calcd for C\textsubscript{66}H\textsubscript{48}Co\textsubscript{2}N\textsubscript{4}O\textsubscript{16}P\textsubscript{2}: C, 49.89; H, 5.66; N, 6.84. Found: C, 49.56; H: 5.24; N, 6.97; FT-IR (KBr, cm\textsuperscript{-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 °C (Weight loss %): 30-270 (1.7); 270-340 (36.8); 340-515(22.4); 515-1000(6.5).

**[Co\textsubscript{3}(dipp)(2-apy)(DMso)(H\textsubscript{2}O)]\textsubscript{2} (7).** A solution of dippH\textsubscript{2} (129.0 mg, 0.5 mmol) in methanol (10 mL) was added to a solution of Co(OAc)\textsubscript{2}-4H\textsubscript{2}O (124.5 mg, 0.5 mmol) in methanol (25 mL). The solution was stirred until it became clear and then solid 2-aminoypyridine (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 kept at x15 mixture under reduced pressure and the blue residue obtained was used for crystallization. Deep blue colour X-ray quality single crystals of compound 7 were isolated after three weeks. M.p: >275 °C. Yield: 14.5 mg (67 %, based on Co). Anal. Calcd for C\textsubscript{128}H\textsubscript{100}Co\textsubscript{3}N\textsubscript{8}O\textsubscript{14}P\textsubscript{2}S\textsubscript{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, cm\textsuperscript{-1}): 3437(br), 3215(w), 3065(w), 2964(m), 2867(m), 1635(s), 1567(m), 1497(s), 1450(m), 1338(w), 1257(w), 1171(vs), 1057(vs), 771(s). TGA: Temp. range °C (% Weight loss): 30-220 (3.3); 220-330 (28.7); 330-500 (29.9); 500-1000(4.8).

**[Co(dipp)(dptz)(S\textsubscript{4}O\textsubscript{6})\textsubscript{2} (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 dippH\textsubscript{2} (12.9 mg, 0.10 mmol) and Co(OAc)\textsubscript{2}-4H\textsubscript{2}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 °C. Yield: 14.5 mg (67 %, based on Co). Anal. Calcd for C\textsubscript{128}H\textsubscript{100}Co\textsubscript{3}N\textsubscript{8}O\textsubscript{14}P\textsubscript{2}S\textsubscript{2}: C, 49.90; H, 4.89; N, 7.97. Found: C, 47.36; H, 4.66; N, 7.79; FT-IR (KBr, cm\textsuperscript{-1}): 3434(br), 2965(m), 2928(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 °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.

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**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, Co(OAc)₄·4H₂O with diph₂ in an appropriate solvent in the presence of different N-donor ancillary ligands followed by slow crystallisation leads to the formation of different mononuclear, 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 diph₂ in methanol, analytically pure pink crystals of the mononuclear compound [Co(dippH)(2-apy)] (1) were obtained in quantitative yield (Scheme 1). The compound possesses a single Co²⁺ 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 monoaonionic phosphate ligands. The free P-OH group remains uncoordinated along with the dangling P=O oxygen atom from the two monoanionic phosphate ligands. The free oxygen atoms of two different bridging phosphate moieties. The Co²⁺ ions are coordinated by three phosphate 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 Co(OAc)₄·4H₂O, diph₂ and 2-aminopyridine in a 1:1:1 molar ratio using methanol as the solvent at room temperature yields the symmetric tetranuclear cluster [Co(dipp)(2-apy)]₄ (6) in quantitative yields. The compound is obtained as deep blue rectangular blocks having a core of Co₈P₄O₁₂ that resembles the double-4-ring (D₄R) zeolite SBU. All four of the Co²⁺ ions in the compound are in a tetrahedral environment. In the D₄R cubane structure, the Co²⁺ 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 Co(OAc)₄·4H₂O, diph₂ 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 [Co₆(dipp)₂(2-apy)₂(DMSO)]₆(DMSO)·(H₂O) (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-dipyrindin-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, diph₂ 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 diph₂ and Co(OAc)₄·4H₂O in DMSO was layered with neat methanol which in turn was layered by a methanol solution of dptz. This method prevented immediate precipitation and lead to the isolation of the cobalt phosphate 3D framework [{Co(dipp)(dptz)₃}₃]₆ (8) (Scheme 2). This method exemplifies a soft approach for the synthesis of 3D frameworks at ambient conditions.

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 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 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 cm⁻¹. However, the infrared spectra of compound 2-8 are devoid of any absorption in the region of 2300 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-butylyphosphate (dtbp) complexes of cobalt, [Co(dtbp)₂]₄²⁺ and [Co₂(O₂)₄(dtbp)₄]₃²⁺d can act as single source precursors for the preparation of either pure Co₃O₄ or a mixture of Co₃P₂O₄·Co₃O₄ 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 shows 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 Co(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 Co$_2$P$_2$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 [CoO$_5$P(OH)] which then eliminates water to form Co$_2$P$_2$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 [CoO$_5$P(OH)], which then eliminates water to leave 27.0 % of the initial mass at 1000 °C, corresponding to ceramic residue of Co$_2$P$_2$O$_7$ (theoretical yield 27.0 %). Compound 6 is stable up to 400 °C after which it decomposes in three steps to form Co$_2$P$_2$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 dpz linkers are lost up to 500 °C resulting in the exclusive formation of Co$_2$P$_2$O$_7$. In summary, apart from 1 (which yields Co(PO$_3$)$_2$), all other molecular phosphates described in the present study show stepwise loss of various organics residues to finally yield the pyrophosphate Co$_2$P$_2$O$_7$.

**Molecular structure of [Co(py)$_2$(dippH)$_2$]$_2$ (1)**

Rectangular pink crystals of 1 were obtained by slow evaporation of a methanol-pyridine mixture of cobalt acetate and dipp$_2$H$_2$ ligand at room temperature after one week. Compound 1 crystallises in the centrosymmetric triclinic space group P$ar{1}$. 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 centres in a unidentate fashion ([1.100] mode - Harris notation) 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. The phosphoryl oxygen atoms are strongly involved in intermolecular interactions with the adjacent units to yield a zigzag 1-D polymeric structure (Figure 2) (O3⋯O4 2.582(2) Å, H3A⋯O4 1.72(4) Å, O3⋯H3A 0.87(4) Å, O3⋯H3A⋯O4 174(3)°). It is worth noting that the structurally similar molecular metal phosphates [M(dtbp)$_2$(imz)$_2$]$_2$ (M = Mn, Co, Ni, Cu, Zn) were reported by us.

**Molecular structure of [Co(dipp)(bpy)(MeOH)$_2$]$_2$·2MeOH (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. Thus, two 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⋯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 π–π stacking between the adjacent molecules involving the symmetry 2,2'-bipyridines (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 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⋯O hydrogen bonding interactions in 1 (all hydrogen atoms except for H3A are omitted for clarity).

**Figure 3.** (a) Molecular structure of 2 (H-atoms are omitted for clarity). (Inset: core structure resembling a S4R unit).
Molecular structure of [Co(dipp)(phen)(MeOH)]$_2$·2MeOH (3)

Red crystals for 3 were grown by the slow evaporation of solvent from the reaction mixture at ambient temperature. Compound 3 crystallizes in the monoclinic space group $\text{P2}_1/n$ 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 $\text{Co}_2\text{P}_2\text{O}_4$ eight-membered ring is enveloped by intramolecular hydrogen bonds (O5–H5W···O3 2.696(2) Å = 171.1(1)$^\circ$; O6–H6W···O3 2.730(2) Å, =169.9(1)$^\circ$) 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.

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)$^\circ$; O7–H7W···O3 = 2.721(3) Å, 172.7(2)$^\circ$) 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)]$_2$·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 $\text{Pbca}$ 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)$^\circ$ and 135.10(2)$^\circ$. 

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).

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).

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)2(dipp)2]_2·2MeOH (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 P1. 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 = 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.

Molecular structure of [Co(dipp)(2-apy)]_4 (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 C2/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-aminoypyridine ligands arranged in the form of a closed cluster in the CoO_5P_2 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_3O_5P_2 core, 17,18 and metallosiloxanes 19 with a M_4O_5Si_4 core. Compounds with this core have assumed particular importance due to their resemblance to the commonly observed D4R (double-fourring) SBU of zeolites and other framework solids. Although first row divalent transition metal ions such as Zn^{2+}, Mn^{2+}, and Cu^{2+} have already been incorporated inside clusters analogous to compound 6, this is the first example of a D4R cobalt phosphate. 20 Each of the Co···P edges of the cube is bridged by a phosphate oxygen in a μ^2 fashion, resulting in the formation of six non-planar Co_2O_6P_2 eight membered rings that adopt a distorted pseudo-C_4 crown conformation. The bridging dipp ligand in 6 binds in a [3.111] mode. 21 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_2 groups in compound 6 forms an intramolecular N–H···O interaction with one of the framework oxygens, two –NH 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 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.
Molecular structure of \([\text{Co}_4(dipp)_4(2\text{-apy})_3(DMSO)]\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
Metal organic frameworks containing nitrogen rich surfaces have been shown to be better scavengers of CO\(_2\) compared to the N-free surfaces.\(^\text{79}\) As the framework material 8 contains bridging ligand dptz with N-atoms, CO\(_2\) adsorption studies were carried out at 273K. The framework material 8 shows a type-II adsorption isotherm for CO\(_2\) (Figure 18) in the lower pressure region up to 1 bar with uptake capacity of 7.80\% wt. The framework does not adsorb N\(_2\) or H\(_2\) at this temperature indicating the highly selective nature of the framework towards CO\(_2\). High pressure gas adsorption isotherms (Figure 19) were carried out at 273K and 278 K shows that the adsorption by the framework saturates at around 15 bar with CO\(_2\) uptake capacities of 18.0 and 15.5\% wt, respectively although higher CO\(_2\) uptake has been previously reported for other MOFs.\(^\text{78}\)

The volume of the unit cell of framework compound 8 is 10057 Å\(^3\) and the framework has a void space of 1285 Å\(^3\) per unit cell. This void can contain 22.05 wt % of CO\(_2\) at 273K, which is slightly higher than the experimental value of 18\% wt. As the adsorbed CO\(_2\) gas cannot be assumed to occupy the whole void space available, the numbers obtained for the maximum uptake of CO\(_2\) at varying pressures are reasonable.

**Figure 18.** CO\(_2\) along with N\(_2\) and H\(_2\) adsorption in the framework of framework 8 at 273 K, showing high selectivity for CO\(_2\).

**Figure 19.** High pressure CO\(_2\) adsorption isotherm at 273K and 298 K for framework 8.

**Magnetic properties of compounds 1-8**

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

Although compounds 2 and 3 both comprise two six-coordinate Co\(^{2+}\) ions bridged by two phosphates, their low temperature magnetic behaviours are markedly different. For 3, both \(\chi T\) and \(M\) are similar to the sum of two independent six-coordinate Co\(^{2+}\) ions (\(\chi T = 3.46\) cm\(^3\)/K mol\(^{-1}\) at 2 K; \(M\) 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, \(\chi T\) for 2 undergoes a sharper downturn below ca. 20 K, reaching 1.30 cm\(^3\)/K mol\(^{-1}\) at 2 K, and \(M\) 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\(^{2+}\) dimers (even antiferro- to ferro-magnetic) on substitution of terminal ligands with no change to the bridging arrangement.\(^\text{80}\)

In contrast to 1-3, complexes 4-8 contain pseudo-tetrahedral Co\(^{2+}\) ions (A ground term), hence their magnetic properties are in principle amenable to treatment with a spin-only Hamiltonian. For the dimetics 4 and 5, \(\chi T\) is ca. 4.5 cm\(^3\)/K mol\(^{-1}\) at room temperature, consistent with the sum of the two \(S = 3/2\) ions with \(g > 2.2\), which decreases with decreasing temperature (Figure 24). For compound 4, \(\chi T\) decreases more rapidly below ca. 10 K, tending towards nil (reaching 0.43 cm\(^3\)/K mol\(^{-1}\) at 2 K). This is consistent with antiferromagnetic coupling between the Co\(^{2+}\) 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 \(M\) 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 behaviour of the
Co$_2$ 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 $\gamma T$ at room temperature is reasonable for the sum of four $S = 3/2$, but with some variation in $g$, and $\gamma T(T)$ decreases on cooling, tending towards nil at base temperatures. In each case, $M(T)$ rises only slowly with $T$ (Figures S14, S15, S19).

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

$$H = \sum_i \frac{g_i \mu_B \vec{S}_i \cdot \vec{H}}{2} - 2J \sum_{i,j=1}^{n} \vec{S}_i \cdot \vec{S}_j \tag{1}$$

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 $\gamma T(T)$, allowing $g$ and $J$ to vary as free parameters, gave: $g = 2.31$, $J = -2.4$ cm$^{-1}$ (4); $g = 2.36$, $J = -1.5$ cm$^{-1}$ (6); $g = 2.23$, $J = -1.4$ cm$^{-1}$ (7); $g = 2.07$, $J = -1.46$ cm$^{-1}$ (8) (Figure 21). These parameters also reproduce the slowly increasing $M(T)$ 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 $M(T)$ data. The most obvious omission is the single ion zero-field splittings, which can be very large for pseudo-tetrahedral Co$^{2+}$ ions.\(^{31}\) 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-metalllics is expected because in both sets of complexes each pair of Co$^{2+}$ 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,\(^{26}\) 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-propylphenylphosphine 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 (dpz) 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 framework, [(Co(dip)(dpz)$_2$)$_2$)$_2$]$_n$ (8). The cobalt organophosphonate framework 8 shows highly selective CO$_2$ adsorption over N$_2$ and H$_2$. The CO$_2$ 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 organophosphonate framework being utilized for CO$_2$ 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 synthesized 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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\footnote{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/}


Discrete and polymeric cobalt organophosphates: Isolation of a 3-D cobalt phosphate framework exhibiting selective CO$_2$ capture

Sandeep K. Gupta et al.

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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$_2$ capture over N$_2$ and H$_2$. 

![Diagram of zeo-type SBU and CO$_2$, N$_2$, H$_2$]