

# Cobalt(II) frameworks of 3,3'-bipyridyl-5,5'-dicarboxylate (bpdc<sup>2-</sup>). X-Ray crystal structures of [Co(bpdc)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> and {[Co(bpdc)(H<sub>2</sub>O)<sub>4</sub>].2H<sub>2</sub>O}<sub>n</sub>

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Sodium 3,3'-bipyridyl-5,5'-dicarboxylate (Na<sub>2</sub>bpdc) reacts with cobalt(II) chloride under hydrothermal conditions to give the guest-free two-dimensional framework [Co(bpdc)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> **1** and at ambient temperature to generate the one-dimensional polymer {[Co(bpdc)(H<sub>2</sub>O)<sub>4</sub>].2H<sub>2</sub>O}<sub>n</sub> **2**. In **1** the bpdc<sup>2-</sup> ligand is tetradentate, coordinating through the pyridyl nitrogens and two of the carboxylate oxygen atoms, in **2** solely the nitrogen atoms of this ligand bind to cobalt.

**Keywords:** metal–organic framework, X-ray crystallography, bipyridyl; dicarboxylate, hydrothermal synthesis, cobalt

Metal–organic frameworks (MOFs) have been the subject of several reviews, which highlight the breadth of organic units from which MOFs can be constructed, the topological motifs encountered in the frameworks and their physicochemical features.<sup>1</sup> Bipyridyl ligands and aromatic polycarboxylic acids are popular building blocks for MOF construction; more recently 2,2'-bipyridyl-*n,n'*-dicarboxylic acids (where *n,n'* are the locants of the acid groups) have attracted considerable interest.<sup>2</sup> With a mixed donor set and the potential for structural variations offered by positional isomerism, these tectons necessarily support different framework architectures to their simpler counterparts. By contrast, MOFs generated from dicarboxylic acid derivatised 3,3'- or 4,4'-bipyridyls are unknown, indeed, few such ligands are documented in the literature; to the best of our knowledge 4,4'-bipyridyl-3,3'-dicarboxylic acid<sup>3a</sup> and 3,3'-bipyridyl-2,2'-dicarboxylic acid<sup>3b</sup> have been reported, but not so far used for MOF preparation. Prohibiting *N,N'*-chelation will alter the inner-sphere arrangements of the metal compared with 2,2'-bipyridyl-*n,n'*-dicarboxylic acid tectons, affecting the dimensionality of the resultant MOF, hence substantial differences in solid-state structures and properties are assured. Moreover, the opportunity to form discrete monomeric complexes, an important feature of the chemistry of 2,2'-bipyridyl-*n,n'*-dicarboxylic acids, is lost with 3,3'-/4,4'-bipyridyl isomers. We report here our use of sodium 3,3'-bipyridyl-5,5'-dicarboxylate (Na<sub>2</sub>bpdc) to prepare frameworks with cobalt(II) at room temperature and under hydrothermal conditions, two representative X-ray crystal structures are presented.

## Experimental

Procedures were performed under aerobic conditions, solvents were used as received. <sup>1</sup>H NMR (300.0 MHz) and IR spectra (pressed KBr pellets) were recorded on Bruker DPX 300 and Nicolet Nexus FTIR/Raman spectrometers respectively, elemental analyses were by the UMIST Microanalytical Service.

**Na<sub>2</sub>bpdc:** A suspension of dimethyl 3,3'-bipyridyl-5,5'-dicarboxylate<sup>4</sup> (0.80 g, 2.9 mmol) and sodium hydroxide (0.29 g, 7.2 mmol) in THF-distilled water (10: 1 v/v, 20 cm<sup>3</sup>) was refluxed for 10 h. Upon cooling to room temperature the colourless precipitate was filtered off, washed with thf (2 × 20 cm<sup>3</sup>) and diethyl ether (2 × 20 cm<sup>3</sup>), then dried *in vacuo*. Yield 0.80 g (96 %). Found (calc. for C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>4</sub>): C 49.2 (50.0), H 2.0 (2.1), N 9.4 (9.7) %. δ<sub>H</sub> (D<sub>2</sub>O): 8.89 (s, 1H), 8.81 (s, 1H), 8.42 (s, 1H). Selected IR bands (cm<sup>-1</sup>): 1626 s, 1379 s (ν<sub>COO</sub>).

**H<sub>2</sub>bpdc:** To Na<sub>2</sub>bpdc (200 mg, 0.7 mmol) in distilled water (7 cm<sup>3</sup>) was added concentrated hydrochloric acid (2–3 drops). The colourless precipitate which formed immediately was filtered off and washed with ethanol (2 × 20 cm<sup>3</sup>) and diethyl ether (2 × 20 cm<sup>3</sup>). Yield 126 mg (74 %). A sample was purified from hot DMSO. Found (calc. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>): C 58.4 (59.0), H 3.5 (3.3), N 10.6 (11.5) %. δ<sub>H</sub> (*d*<sub>c</sub>-DMSO): 9.19 (s, 1H), 9.12 (s, 1H), 8.56 (s, 1H). Selected IR bands (cm<sup>-1</sup>): 3434 m, 3073 m, 2454 m, 1888 m, br (ν<sub>OH</sub>), 1728 s (ν<sub>COO</sub>).

**[Co(bpdc)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> **1**:** Solutions of Na<sub>2</sub>bpdc (100 mg, 0.35 mmol) and anhydrous cobalt(II) chloride (47 mg, 0.35 mmol) in distilled water (10 cm<sup>3</sup>) were mixed and heated at 120 °C under autogenous pressure in a Teflon<sup>®</sup>-lined stainless steel autoclave for 24 h. Upon cooling to room temperature over *ca* 10 min the cherry-pink microcrystals were filtered off and washed with ethanol (2 × 20 cm<sup>3</sup>) and diethyl ether (2 × 20 cm<sup>3</sup>). Yield 85 mg (72 %). Found (calc. for C<sub>12</sub>H<sub>10</sub>CoN<sub>2</sub>O<sub>6</sub>): C 42.7 (42.7), H 2.7 (3.0), N 8.3 (8.3) %. Selected IR bands (cm<sup>-1</sup>): 1633 s, 1380 s (ν<sub>COO</sub>).

**{[Co(bpdc)(H<sub>2</sub>O)<sub>4</sub>].2H<sub>2</sub>O}<sub>n</sub> **2**:** Crystals were grown at room temperature over 72 h by layering an ethanolic solution of anhydrous cobalt(II) chloride onto an aqueous solution of Na<sub>2</sub>bpdc (both concentrations were typically 2–5 mmol dm<sup>-3</sup>). Bulk quantities of **2** (as a tetrahydrate) were isolated in non-crystalline form by mixing aqueous solutions of the precursors, filtering off the pink precipitate and washing with ethanol (2 × 20 cm<sup>3</sup>) and diethyl ether (2 × 20 cm<sup>3</sup>). Yield 54 %. Found (calc. for C<sub>12</sub>H<sub>14</sub>CoN<sub>2</sub>O<sub>8</sub>.4H<sub>2</sub>O): C 32.6 (32.4), H 4.6 (5.0), N 6.2 (6.3) %. Selected IR bands (cm<sup>-1</sup>): 3244 s, br (ν<sub>OH</sub>), 1612 s, 1376 s (ν<sub>COO</sub>).

## X-Ray crystallography

Single crystal X-ray diffraction studies were performed using a Nonius κ-CCD four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods, non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms bound to carbon were idealised and fixed (C–H 0.94 Å). Hydrogen atoms belonging to water molecules were located from Fourier difference maps and refined isotropically. Structural refinements were by the full-matrix least-squares method on *F*<sup>2</sup> using SHELXTL,<sup>5</sup> absorption corrections were made by the multi-scan method using SORTAV.

**1:** C<sub>12</sub>H<sub>10</sub>CoN<sub>2</sub>O<sub>6</sub>, *T* = 200(2) K, *M* = 337.15, monoclinic, space group *C2/c*, *a* = 12.9150(7) Å, *b* = 7.4386(5) Å, *c* = 12.0353(6) Å, β = 98.277(5)°, *U* = 1144.18(11) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.957 Mg m<sup>-3</sup>, μ = 1.534 mm<sup>-1</sup>, *F*(000) = 684. Of 3864 measured data, 1049 were unique (*R*<sub>int</sub> = 0.0539) to give *R*1[*I* > 2σ(*I*)] = 0.0345, *wR*2 = 0.0795.

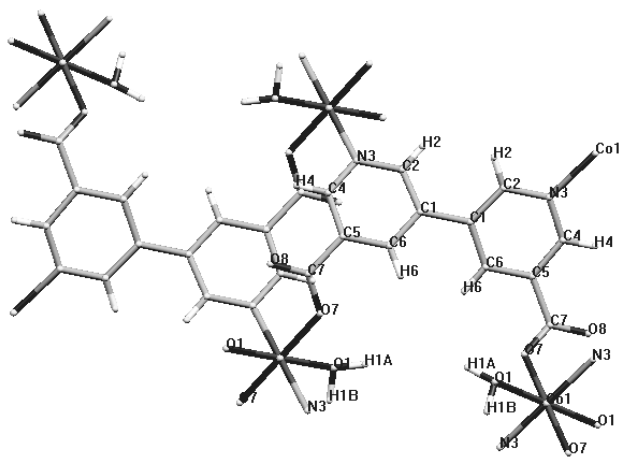
**2:** C<sub>12</sub>H<sub>18</sub>CoN<sub>2</sub>O<sub>10</sub>, *T* = 223(2) K, *M* = 409.07, triclinic, space group *P*(-1), *a* = 11.5439(4) Å, *b* = 11.7317(4) Å, *c* = 13.5571(5) Å, α = 67.2740(10)°, β = 72.757(2)°, γ = 77.826(2)°, *U* = 1607.67(10) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.690 Mg m<sup>-3</sup>, μ = 1.125 mm<sup>-1</sup>, *F*(000) = 844. Of 19751 measured data, 5646 were unique (*R*<sub>int</sub> = 0.0545) to give *R*1[*I* > 2σ(*I*)] = 0.0461, *wR*2 = 0.1102.

Crystallographic data deposited at the Cambridge Crystallographic Database Centre as CCDC-263450 (**1**), 263451 (**2**) can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

## Results and discussion

Hydrolysis of dimethyl 3,3'-bipyridyl-5,5'-dicarboxylate (Me<sub>2</sub>bpdc)<sup>4</sup> with sodium hydroxide affords Na<sub>2</sub>bpdc in high yield. The sodium salt is moderately water-soluble,

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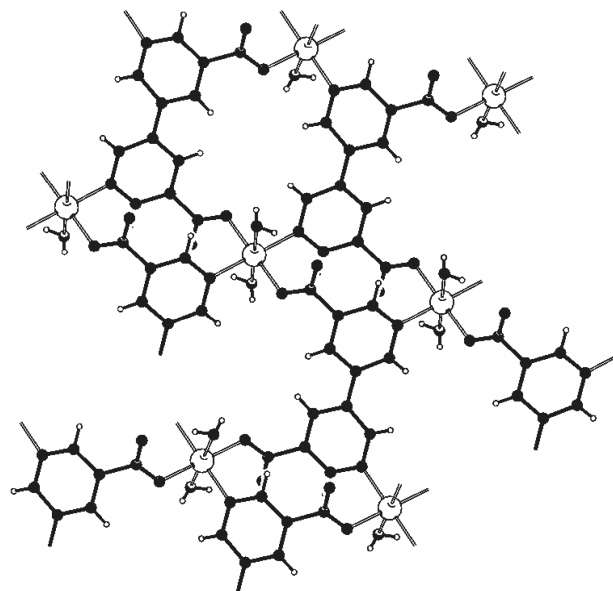


**Fig. 1** Molecular structure and atomic numbering scheme for **1**. Selected bond angles (Å) and angles (°); Co1–O1<sup>iv</sup> 2.306(2), Co1–O7<sup>iv</sup> 2.028(2), Co1–N3<sup>ii,iii,v</sup> 2.020(2), N3<sup>ii</sup>–Co1–N3<sup>iii</sup> 180.00, N3<sup>ii</sup>–Co1–O7 90.69(9), N3<sup>iii</sup>–Co1–O7 89.31(9), O7–Co1–O7<sup>iv</sup> 180.0, N3<sup>ii</sup>–Co1–O1<sup>iv</sup> 90.93(9), N3<sup>ii</sup>–Co1–O1<sup>i</sup> 89.07(9), O1<sup>iv</sup>–Co1–O1 180.0, O7–Co1–O1 92.74(9), O7–Co1–O1<sup>iv</sup> 87.26(9). Symmetry transformations used to generate equivalent atoms: (i)  $-x, y, -z + 1/2$ ; (ii)  $-x + 1/2, -y + 3/2, -z + 1$ ; (iii)  $x, y + 1, z$ ; (iv)  $-x + 1/2, -y + 5/2, -z + 1$ ; (v)  $x, y - 1, z$ .

acidification of an aqueous solution of the salt with hydrochloric acid gives H<sub>2</sub>bpdc, which is sparingly soluble in DMSO. Neither compound has been accessible in a sufficiently crystalline form for X-ray crystallographic analysis.

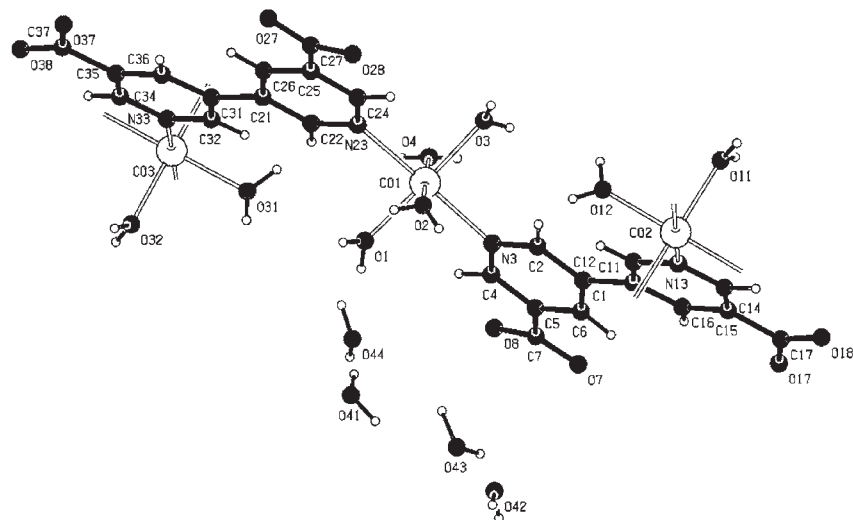
The framework [Co(bpdc)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> **1** was prepared under hydrothermal conditions at 120 °C from equimolar amounts of Na<sub>2</sub>bpdc and anhydrous cobalt(II) chloride; **1** is an air-stable pink microcrystalline solid which is insoluble in organic or inorganic media. Nickel(II) and copper(II) analogues of **1** are available only as non-crystalline powders under identical conditions. X-ray crystallographic analysis (Fig. 1) shows that in **1** the pseudo-octahedral coordination sphere about Co1 comprises two nitrogen atoms and two carboxylate oxygens in the equatorial plane from bpdc<sup>2-</sup> ligands and two axially situated water molecules, with an all *trans*- geometry. The bpdc<sup>2-</sup> ligands bind four cobalt(II) centres through both of the pyridyl nitrogens and two of the carboxylate oxygen atoms. The metal centres and bpdc<sup>2-</sup> ligands act as 4-connectors in the ruffled two-dimensional sheets (Fig. 2). Within the layers the neighbouring cobalt-to-cobalt distances are 7.439 and 8.168 Å, between adjacent layers the shortest Co...Co separations are 7.452 Å. The Co1–N1 and Co1–O7(bpdc) lengths [2.020(2) and 2.028(2) Å respectively] are shorter than in 2,2'-bipyridyl-*n,n'*-dicarboxylate frameworks of Co(II),<sup>2b,2c,2e,2h</sup> conversely the Co1–O1(water) distance [2.306(2) Å] is unusually long, the angles between *cis*- ligands are in the range 87.26(9)–92.74(9)°. Within the bpdc<sup>2-</sup> ligands the pyridyl rings twist about the central C1–C1' bond with a dihedral angle of 32° from the *anti* conformation, similar to the distortions found in 2,2'-bipyridyl-4,4'-dicarboxylate frameworks of *d*-block metals,<sup>2c,2d,2h,2i</sup> also the carboxylate and pyridyl planes twist about C5–C7 by *ca* 30° to one another. The unbound carbonyl oxygen atoms (O8) of the carboxylate groups participate in hydrogen-bonding interactions with the aqua ligands (H1A...O8 1.851 Å, O1...O8 2.753 Å, O1–H1A...O8 170°; H1B...O8' 1.904 Å, O1...O8' 2.786 Å, O1–H1B...O8' 149°).

Crystals of {[Co(bpdc)(H<sub>2</sub>O)<sub>4</sub>].2H<sub>2</sub>O}<sub>n</sub> **2** were grown by slow diffusion of an ethanolic solution of anhydrous cobalt(II) chloride into an aqueous solution of Na<sub>2</sub>bpdc. Millimolar concentrations of the reagents were used to avoid rapid precipitation of the bulk material {[Co(bpdc)(H<sub>2</sub>O)<sub>4</sub>].4H<sub>2</sub>O}<sub>n</sub> and to deliver X-ray quality crystals. Within **2** the pseudo-

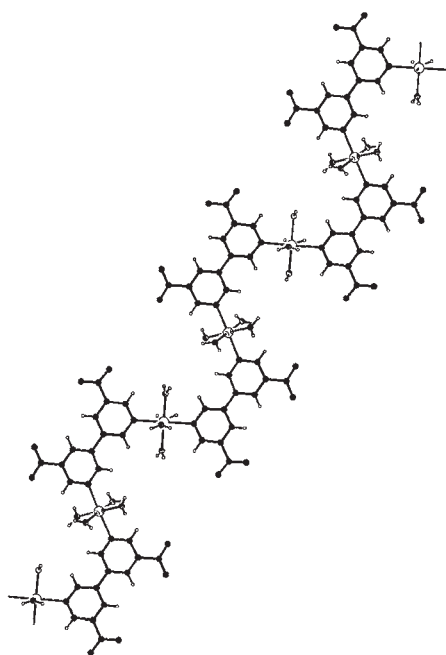


**Fig. 2** The two-dimensional sheets in **1**.

octahedral metal centres are linked into (theoretically infinite) one-dimensional chains by axially coordinated nitrogen atoms from bpdc<sup>2-</sup>, four water molecules in the equatorial plane completing the N<sub>2</sub>O<sub>4</sub> inner sphere (Figs 3, 4). The carboxylate oxygens are uninvolved in metal binding, which is an artefact of the room temperature crystallisation. There is a limited number of crystallographically-characterised 2,2'-bipyridyl-*n,n'*-dicarboxylate complexes in which non-coordination of either the nitrogen atoms<sup>6a,6b</sup> or the carboxylate groups<sup>2c,6c,6d</sup> occurs, the majority of which were crystallised at room temperature. The chains in **2** have a zig-zag character, analogous to the related structures [CoCl<sub>2</sub>(4,7-phenanthroline)]<sub>n</sub> and [{Co(3,3'-bipy)<sub>2</sub>}]<sub>2</sub>V<sub>4</sub>O<sub>12</sub>]<sub>n</sub>.<sup>7,8</sup> The chains intermesh along the crystallographic *b*-axis and within adjacent chains the centroids of the pyridyl rings are offset from one another, the closest distance between pyridyl ring atoms being *ca* 3.5 Å. There are three crystallographically inequivalent metal centres with a ...Co1...Co2...Co1...Co3... repeating pattern; Co2 and Co3 lie on crystallographic inversion centres and for Co1 the coordination geometry is non-centrosymmetric. The difference in donor sets between **1** and **2** profoundly influences the cobalt–ligand distances. The Co–N lengths in **2** [2.1852(7)–2.2158(9) Å] are  $\approx$  0.16–0.19 Å longer than in **1**, whereas the Co–O<sub>water</sub> distances [2.0435(9)–2.0996 Å] are  $\approx$  0.20–0.25 Å shorter than in **1**. The *cis*- and *trans*- angles are in the ranges 85.68(3)–93.74(3)° and 176.60(3)–180.0°, with the largest distortions being at Co1. The pyridyl rings twist about the central C–C bond with dihedral angles of 7.6–15.6°, substantially reduced from **1**, while the carboxylate group and pyridyl ring planes are nearly coplanar with one another (dihedral angles  $\approx$  0–10°). The intrachain cobalt-to-cobalt distances are 7.854–8.037 Å, comparable with **1**. An O–H...O hydrogen-bonding network encompasses the pendant carboxylate groups, aqua ligands and lattice water molecules, these guests occupying channels running along the crystallographic *b*-axis. Among the aqua ligands the O3 molecule at Co1 uniquely acts as both a donor and an acceptor, for the lattice water molecules O43 hydrogen-bonds only with other guests whereas O41, O42 and O44 also interact with aqua ligands and carboxylate groups. The H...O distances are in the range 1.795(12)–1.985(12) Å for the aqua ligands and 1.91–2.59 Å for the lattice water molecules.



**Fig. 3** Molecular structure and atomic numbering scheme for **2**. Selected bond angles (Å) and angles (°); Co1–O1 2.0435(9), Co1–O2 2.0629(8), Co1–O3 2.0728(8), Co1–O4 2.0796(8), Co1–N23 2.1852(7), Co1–N3 2.1934(7), Co2–O12 2.0801(6), Co2–O11 2.0932, Co2–N13 2.2065(9), Co3–O32 2.0716, Co3–O31 2.0996, Co3–N33 2.2158(9), O1–Co1–O2 90.55(3), O1–Co1–O3 176.60(3), O2–Co1–O3 91.90(3), O1–Co1–O4 91.84(4), O2–Co1–O4 177.52(4), O3–Co1–O4 85.68(3), O1–Co1–N23 86.56(3), O2–Co1–N23 85.75(3), O3–Co1–N23 91.28(3), O4–Co1–N23 93.74(3), O1–Co1–N3 92.75(3), O2–Co1–N3 91.33(3), O3–Co1–N3 89.54(3), O4–Co1–N3 89.21(3), N23–Co1–N3 176.99(3), O12<sup>i</sup>–Co2–O12 180.0, O12<sup>i</sup>–Co2–O11 90.99(3), O12–Co2–O11 89.01(3), O11–Co2–O11<sup>i</sup> 180.0, O12–Co2–N13<sup>i</sup> 91.07(3), O11–Co2–N13<sup>i</sup> 89.57(3), O12–Co2–N13 88.93(3), O11–Co2–N13 90.43(3), N13<sup>i</sup>–Co2–N13 180.0, O32<sup>ii</sup>–Co3–O32 180.0, O32–Co3–O31 88.2, O32–Co3–O31<sup>ii</sup> 91.8, O31–Co3–O31<sup>ii</sup> 180.0, O32–Co3–N33<sup>ii</sup> 90.63(3), O31–Co3–N33 89.84(3), O31<sup>ii</sup>–Co3–N33 90.16(3), O32–Co3–N33<sup>iii</sup> 89.37(3), N33–Co3–N33<sup>iii</sup> 180.00(4). Symmetry transformations used to generate equivalent atoms: (i)  $-x + 1, -y + 1, -z$ ; (ii)  $-x, -y + 2, -z + 2$ .



**Fig. 4** The one-dimensional chains in **2**.

### Summary and conclusions

Under hydrothermal conditions the coordination of the pyridyl nitrogen atoms and carboxylate groups of  $\text{bpdC}^{2-}$  to cobalt(II) occurs in the guest-free two-dimensional framework  $[\text{Co}(\text{bpdC})(\text{H}_2\text{O})_2]_n$  **1**, while at room temperature  $\{[\text{Co}(\text{bpdC})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$  **2** is afforded, in which the cobalt centres are linked into chains by the nitrogen atoms of  $\text{bpdC}^{2-}$ , the carboxylate groups being innocent. This difference in behaviour as a function of temperature resembles the chemistry of the more widely studied 2,2'-bipyridyl- $n,n'$ -dicarboxylic acid derivatives. Using other  $d$ - and  $f$ -block ions will undoubtedly provide a broad spectrum of structural features (e.g. dimensionality, pore size, donor sets) for

the resultant MOFs, Kruger's observations of network isomerisation induced by synthesis in different solvents<sup>2d</sup> may well find parallel with isomers of  $\text{bpdC}^{2-}$ .

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