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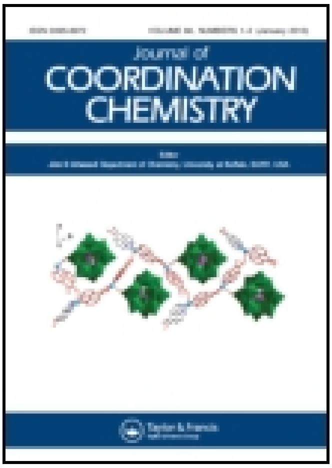

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2-D coordination polymers of copper and cobalt with 3,4-pyridinedicarboxylic acid: synthesis, characterization, and crystal structures

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2-D coordination polymers of copper and cobalt with 3,4-pyridinedicarboxylic acid: synthesis, characterization, and crystal structures

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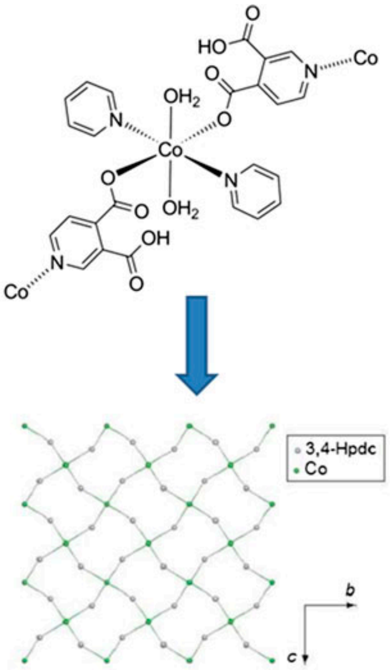

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Two new complexes involving 3,4-pyridinedicarboxylic acid (3,4-H_2pdc), copper(II) and cobalt(II) complexes, $\{[Cu(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2dmso\}_n$ (**1**) and $\{[Co(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2H_2O\cdot 2dmso\}_n$ (**2**) (dmso = dimethylsulfoxide), have been synthesized by the diffusion method and characterized by elemental analysis, IR spectroscopy, thermal analysis, powder and single-crystal X-ray diffraction analysis, and electron paramagnetic resonance (EPR). In both compounds, the metal coordination sphere is composed of a *trans*-MO_4N_2 core and adopts a distorted octahedral geometry in accordance with X-ray diffraction and EPR results. 3,4-$Hpdc^-$ ligands bridge the metal centers giving two-dimensional (2-D) coordination polymers with four-connected uninodal nets of (*4*,*4*) topology.

Keywords: Coordination polymer; 3,4-pyridinedicarboxylic acid; Crystal structure

1. Introduction

Solid engineering is of interest for both structural and topological innovations of organic–inorganic frameworks due to their potential applications in material science as catalytic, conductive, luminescent, magnetic, nonlinear optical, or porous devices [1–5]. Coordination polymer design depends not only on the chosen metals and organic linkers but also on the reaction conditions like temperature, solvents, and counter ions. Polycarboxylate ligands have been often used as good building blocks to construct transition metal or lanthanide coordination polymers [6–16]. In this ligand class, positional isomers of pyridinedicarboxylate anions, such as 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-pdc^{2-} (chart 1), are representative of hybrid spacers (N,O-donors), frequently applied to achieve varied coordination polymers or metal–organic frameworks within supramolecular arrangements [17]. The presence of both pyridine and carboxylate functionalities gives these ligands versatile coordination modes toward different metal ions [8, 18–21], including the formation of heterobimetallic compounds [22, 23].

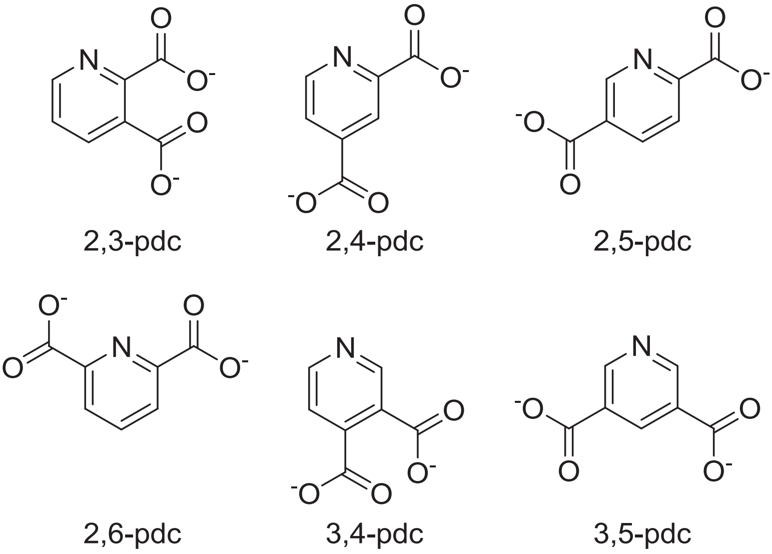

Chart 1. Positional isomers of pyridinedicarboxylate anions.

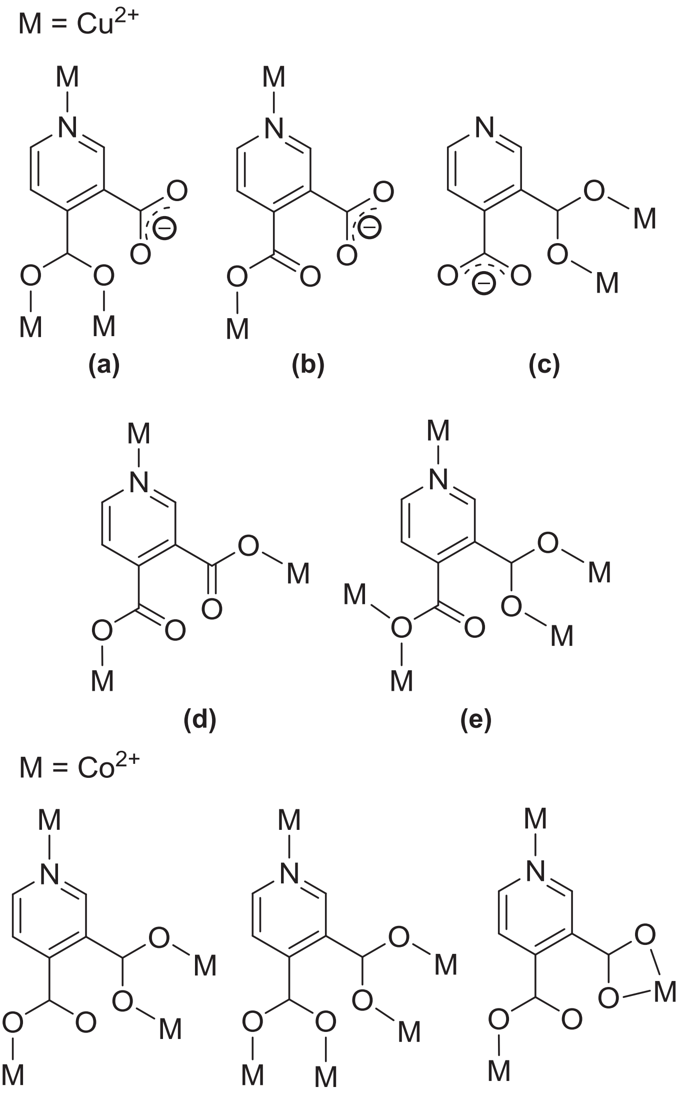

Chart 2. Coordination modes of the 3,4-pdc^{2-} anion toward Cu(II) and Co(II) metal centers.

Especially, the multifunctional ligand 3,4-pyridinedicarboxylic acid (3,4-H_2pdc), also known as cinchomeronic acid, an asymmetric molecule containing five coordination sites, is an excellent building block and, therefore, it has been extensively employed in the construction of metal–organic frameworks [15], in which different coordination modes have been observed toward transition metals and lanthanides [14, 24]. Since compounds with Cu(II) and Co(II) metal centers are described herein, chart 2 presents the coordination modes of the 3,4-pdc^{2-} anion toward these metal ions [25–29]. Because of the ability to make multiple connections, the 3,4-pdc^{2-} ligand can form coordination polymers with different structures and topologies. Due to steric hindrance between the carboxylic groups in the 3- and 4-positions, the participation of only one carboxylic group in coordination to the metal center is expected. However, the rotational freedom of the carboxylic groups makes them flexible enough to participate in the coordination environment at the same time, as reported [14, 20].

In this work, we report the syntheses, characterization, crystal structures, and electron paramagnetic resonance (EPR) studies of 2-D coordination polymers containing the 3,4-Hpdc$^-$ ligand, $\{[Cu(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2dmso\}_n$ (**1**) and $\{[Co(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2H_2O\cdot 2dmso\}_n$ (**2**).

2. Experimental

2.1. *Materials and physical measurements*

All reagents and solvents employed are commercially available and were used as received. C, H, and N elemental analyses were carried out using a PerkinElmer 2400 CHN analyzer. Thermal analysis (TG/DTA) was performed under nitrogen (flow rate = 100 mL min^{-1}) with a heating rate of 10 °C min^{-1} using a DTG60-Shimadzu thermal analyzer. Fourier transform infrared spectra were recorded at ambient conditions using KBr pellets from 4000 to 400 cm^{-1} on a Bomen MB102 spectrophotometer with an average of 64 scans and 4 cm^{-1} of spectral resolution. EPR spectra were measured on finely powdered polycrystalline samples in quartz tubes (Wilmad) and were performed with a custom-built X-band spectrometer working with a commercial, cylindrical Bruker cavity and Varian klystron source and Varian magnet (0–800 mT). For low temperatures, an Oxford flux cryosystem was used (4–300 K). Magnetic field calibration was done with a 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard (g = 2.0037) and frequency measurements with a digital PTS frequency meter. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance DAVICI X-ray diffractometer using Cu-Kα radiation (λ = 1.5418 Å), operating at 40 kV and 40 mA at room temperature.

2.2. *Synthesis of* $\{[Cu(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2dmso\}_n$ *(1)*

The 3,4-H_2pdc (84 mg, 0.5 mM) was dissolved in dmso and was added, through the diffusion method, to an ethanol solution of $CuCl_2\cdot 6H_2O$ (43 mg, 0.25 mM). The resulting green solution was set aside, and after three weeks the solution color changed to blue. Blue crystals of **1** (44 mg, 66% yield) suitable for X-ray diffraction analysis were collected by filtration and washed with dmso. Anal. Calcd for $C_{18}H_{24}N_2O_{12}S_2Cu$ (%): C, 36.77; H, 4.11; N, 4.76. Found (%): C, 36.82; H, 4.11; N, 4.66. IR (KBr, cm^{-1}): 3458 (broad), 3063 (w), 1714 (m), 1639 (m), 1555 (m), 1372 (s), 1279 (m), 1157 (w), 1114 (m), 1078 (w), 1003 (m), 947 (m), 852 (w), 813 (m), 678 (m).

2.3. *Synthesis of* $\{[Co(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2H_2O\cdot 2dmso\}_n$ *(2)*

Compound **2** was obtained through the same method as applied for **1**, replacing the copper salt by $Co(NO_3)_2\cdot 6H_2O$ (178 mg, 0.75 mM). The resulting pink solution was set aside, and after one month, pink crystals of **2** (36 mg, 20% yield) suitable for X-ray diffraction analysis were collected by filtration and washed by dmso. Anal. Calcd for $C_{18}H_{28}N_2O_{14}S_2Co$ (%):

Table 1. Crystal, data collection, and structure refinement parameters for $\{[Cu(3,4\text{-Hpdc})_2(H_2O)_2]\cdot 2dmso\}_n$ (**1**) and $\{[Co(3,4\text{-Hpdc})_2(H_2O)_2]\cdot 2H_2O\cdot 2dmso\}_n$ (**2**).

Compound	**1**	**2**
Empirical formula	$C_{18}H_{24}N_2O_{12}S_2Cu$	$C_{18}H_{28}N_2O_{14}S_2Co$
Formula weight ($g\,M^{-1}$)	588.05	619.47
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	8.8311(7)	8.2952(7)
b (Å)	11.0546(7)	12.5326(6)
c (Å)	12.8617(7)	13.6203(7)
$\alpha = \gamma$ (°)	90	90
β (°)	104.586(7)	105.379(6)
Volume (Å^3)	1215.15(14)	1365.27(15)
Z	2	2
Density ($g\,cm^{-3}$)	1.607	1.507
Reflections collected	12,065	13,718
Independent reflections	1758	2062
S	1.016	1.033
$R[I > 2\sigma(I)]$	0.0438	0.0529
wR	0.0905	0.1283

C, 34.90; H, 4.56; N, 4.52. Found (%): C, 35.09; H, 4.65; N, 4.51. IR (KBr, cm^{-1}): 3472 (broad), 3074 (w), 1718 (s), 1634 (s), 1551 (w), 1315 (m), 1281 (m), 1161 (w), 1117 (m), 1070 (w), 997 (m), 949 (m), 862 (m), 800 (m), 681 (m), 609 (w).

2.4. *Single-crystal X-ray diffraction*

Single-crystal X-ray data were collected using an Oxford GEMINI A Ultra diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at room temperature (298 K). Data collection, reduction, and cell refinement were performed by the CrysAlis RED, Oxford diffraction – Version 1.171.32.38 program [30]. Final unit-cell parameters were based on the fitting of all reflections. The structures were solved by direct methods using SHELXL-97 [31]. An empirical isotropic extinction parameter x was refined according to the method described by Larson [32]. A multiscan absorption correction was applied [33]. The positions of all atoms could be unambiguously assigned by consecutive difference Fourier maps. Refinements were performed using the SHELXL-97 [31] program based on F^2, through a full-matrix least -squares routine. O-bound hydrogens were initially located by a difference Fourier map and were then added in idealized positions and further refined according to a riding model, with O–H = 0.82 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. C-bound hydrogens were included in the riding-model approximation, with C–H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The structures were drawn by the Mercury program [34]. Crystal, data collection, and structure refinement parameters are summarized in table 1.

3. Results and discussion

3.1. *Synthesis and general characterization*

$\{[Cu(3,4\text{-Hpdc})_2(H_2O)_2]\cdot 2dmso\}_n$ (**1**) and $\{[Co(3,4\text{-Hpdc})_2(H_2O)_2]\cdot 2H_2O\cdot 2dmso\}_n$ (**2**) were synthesized by reaction between 3,4-pyridinedicarboxylic acid (3,4-H_2pdc) and

$CuCl_2{\cdot}6H_2O$ (for **1**) and $Co(NO_3)_2{\cdot}6H_2O$ (for **2**) using the diffusion method. Elemental analyses indicated a metal : ligand molar ratio of 1 : 2 in both cases, suggesting that the ligand was partially deprotonated to $Hpdc^-$ to balance the charge. The literature reports various compounds obtained from the reaction between different metal ions (Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Eu^{3+}, Tb^{3+}, U^{6+}) and 3,4-H_2pdc [14, 35–44], and in some of them, an ancillary nitrogen-based ligand such as 1,10-phenanthroline, 4,4′-bipyridine, thiabendazole, 1,3-bis(4-pyridyl)propane, and 1,2-bis(4-pyridyl)ethane was used [45–48]. In most cases, the syntheses were carried out under hydro/solvothermal conditions and also in the presence of a base (NaOH, NEt_3), resulting in products in which the ligand is completely deprotonated (3,4-pdc^{2-} anion). There are two exceptions described in the literature, a 3-D anionic porous coordination net $(NMe_4)_{2n}[Cu_3(\mu_3\text{-}3,4\text{-pdc})_4(H_2O)_4]_n{\cdot}4nH_2O$ [26] and 2-D coordination networks with the general formula $[Ln(3,4\text{-pdc})(3,4\text{-N-Hpdc})]_n$ (Ln = La, Ce, Pr) [35]. In the copper compound synthesis, the diffusion method was used, however, the base $(NMe_4)OH$ was added to the mixture, causing total deprotonation of the ligand. On the other hand, in lanthanoid compounds, a standard Na_2(3,4-pdc) aqueous solution was used as precursor, and the syntheses were performed using a conventional method (stirring and heating), resulting in products containing the totally deprotonated 3,4-pdc^{2-} anion and the 3,4-N-$Hpdc^-$ anion, in which the pyridyl N is protonated. Unlike all these examples, no base was added in the syntheses of **1** and **2**, and mild conditions were used (diffusion method), providing products with the partially deprotonated 3,4-$Hpdc^-$ ligand that, to the best of our knowledge, has never been observed before for 3,4-H_2pdc.

The thermal behaviors of **1** and **2** were evaluated by TG/DTA (figure 1). For **1**, the first weight loss of 6.12 wt%, which occurs from 67 to 100 °C as an endothermic event, corresponds to the release of the two coordinated waters (Calcd, 6.12 wt%). A second weight loss from 158 to 166 °C, also as an endothermic event, was observed and indicates the release of one dmso (Obsd, 12.64 wt%, Calcd, 13.26 wt%). For the third weight loss, at 234–296 °C, we propose, as based on the literature [10], that a C–C bond in the two 3,4-$Hpdc^-$ ligands is broken, generating two C_5H_3NCOOH fragments, corresponding to the weight loss of 51.81 wt% (Calcd, 55.28 wt%) in an endothermic step. The remaining $Cu(COO)_2$ moiety probably decomposed in the final step, a strong exothermic event from 308 to 435 °C, forming carbon dioxide and carbon monoxide (Obsd 11.81 wt%; Calcd, 12.28 wt%). The residual mass at 500 °C is consistent with CuO (Obsd, 12.58 wt%, Calcd, 13.53 wt%). For **2**, the first weight loss of 10.85 wt% occurred around 100 °C as an endothermic event and corresponds to the release of four waters (Calcd, 11.62%). The TGA profile for **2** shows a slow and continuous weight loss of 78.86 wt% from 110 to 426 °C, as

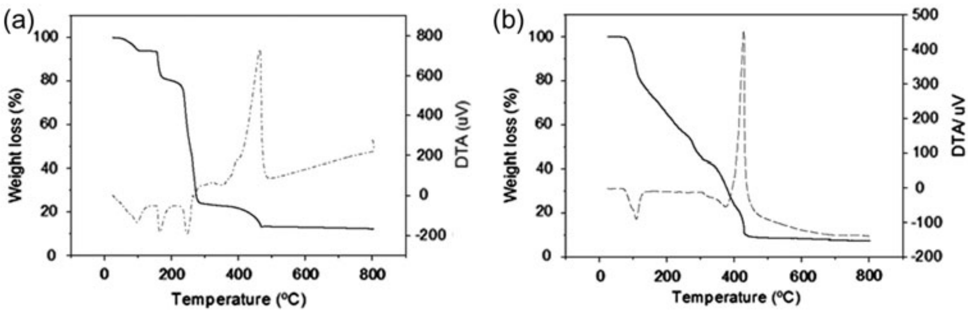

Figure 1. TG and DTA curves of **1** (a) and **2** (b) under a N_2 atmosphere.

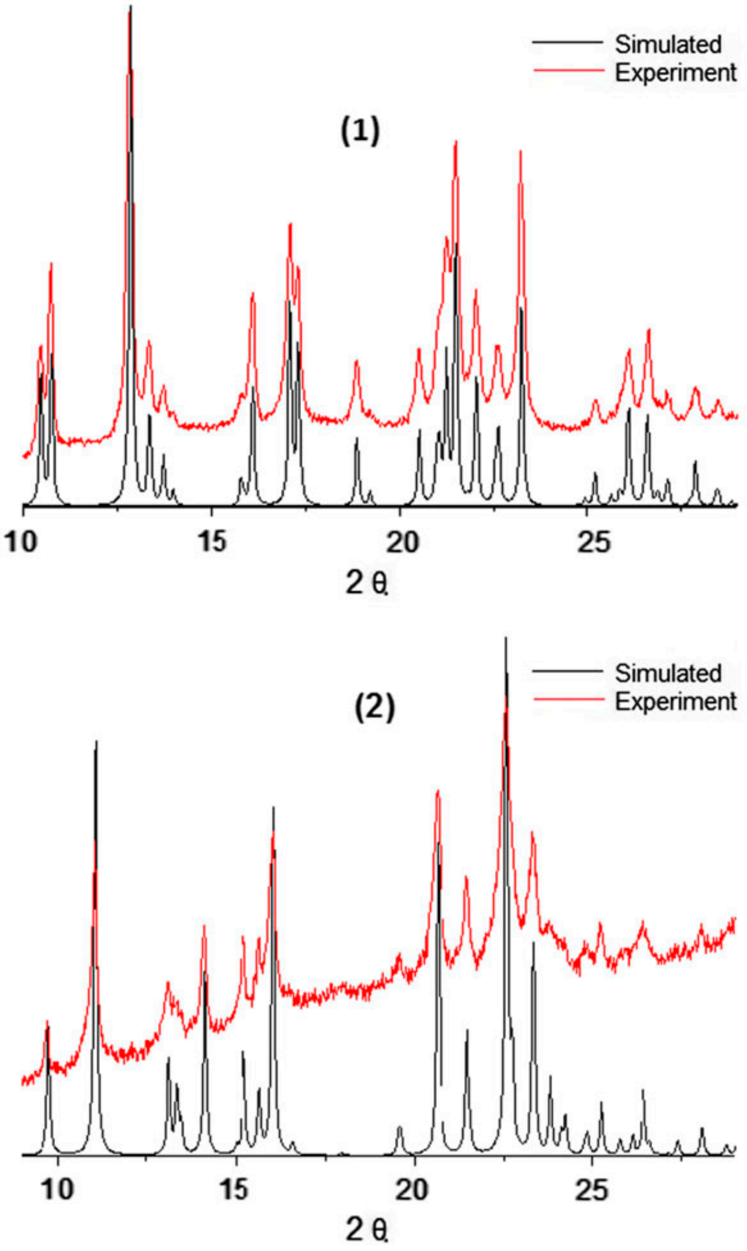

Figure 2. Experimental and simulated PXRD patterns for **1** and **2**.

endothermic and strong exothermic events, attributed to the release of dmso and the ligand decomposition (Calcd, 78.78 wt%). The residue of 9.12 wt% corresponds to the Co percentage in the complex (Calcd, 9.51 wt%).

Infrared spectra of **1** and **2** (figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.959002) show broad bands at 3458 and 3474 cm^{-1}, respectively, attributed to v(OH) of water. Strong absorptions at 1714 and 1718 cm^{-1} for **1** and **2**, respectively, were assigned to v(CO) of the carboxylic acid groups. Other strong absorptions at 1639 and 1372 cm^{-1} for **1** and 1634 and 1402 cm^{-1} for **2** were attributed to v_{as}(COO$^-$) and v_s(COO$^-$), respectively. The presence of v(CO) and v(COO$^-$) indicates that the ligand is partially deprotonated with only one carboxylate coordinated to the metal center. The difference between the asymmetric and symmetric carboxylate stretching frequencies ($\Delta = v_{as}(\mathrm{COO}^-) - v_s(\mathrm{COO}^-)$) is often used to correlate the carboxylate coordination mode [10, 49]. The free ligand has Δ = 223 cm^{-1}, and the Δ values for **1** and **2** are 267 and 232 cm^{-1}, respectively, suggesting monodentate coordination of carboxylate in both compounds.

In addition, bands at 1555 and 1551 cm^{-1} for **1** and **2**, respectively, may be attributed to the pyridyl stretches v(CC/CN). These bands are shifted to higher wavenumbers when compared to the free ligand (1525 cm^{-1}), suggesting the coordination of the pyridyl N to the metal center [50]. Bands at 1078 and 1070 cm^{-1} for **1** and **2**, respectively, were assigned to v(SO) of the sulfoxide group, indicating the presence of dmso in the structures.

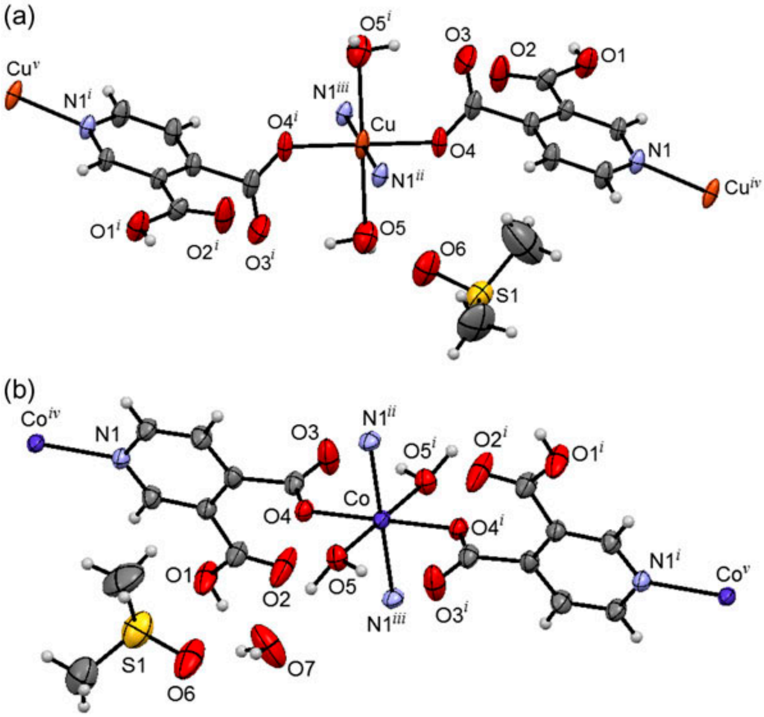

Figure 3. ORTEP diagrams of (a) compound **1**- Symmetry codes: $i = 2 - x, -y, 2 - z$; $ii = 1.5 - x, ½ + y, 1.5 - z$; $iii = ½\,x, -½ -y, ½ + z$; $iv = 1.5 - x, -½ + y, 1.5 - z$; $v = 2 - x, -y - 1, 2 - z$; $vi = ½ + x, -½ - y, -½ + z$. Bond distances (Å): Cu1–O4 = 1.977(2); Cu1–O5 = 2.467(3); Cu1–N1^{ii} = 2.006(2). Bond angles (°): O4^i–Cu1–N1^{ii} = 89.77(10); O4–Cu1–N1^{iii} = 90.23(10); O4–Cu1–O5 = 84.99(10); O4-Cu1–O5^i = 95.01(15); N1^{ii}–Cu1–O5 = 88.00(10); N1^{iii}–Cu1–O5 = 92.00(10). (b) Compound **2** symmetry codes: $i = 2 - x, -y, 2 - z$; $ii = 2 - x, ½ + y, 2.5 - z$; $iii = x, -½ - y, -½ + z$; $iv = 2 - x, -½ + y, 2.5 - z$; $v = x + 1, y, z$; $vi = -x + 2, -y - 1, -z + 2$. Bond distances (Å): Co1–O4 = 2.108(2); Co1–O5 = 2.094(2); Co1–N1 = 2.166(2). Bond angles (°): O4–Co1–O5 = 86.78(9); O5^i–Co1–O4 = 93.20(9); O4–Co1–N1^{ii} = 90.91(9); O4–Co1–N1^{iii} = 89.09(9); O5–Co1–N1^{iii} = 92.27 (10); O5–Co1–N1^{ii} = 87.73(10). Displacement ellipsoids are drawn at the 50% probability level. Only one lattice dmso molecule is shown for **1**, and only one lattice dmso and one lattice water molecule are shown for **2**.

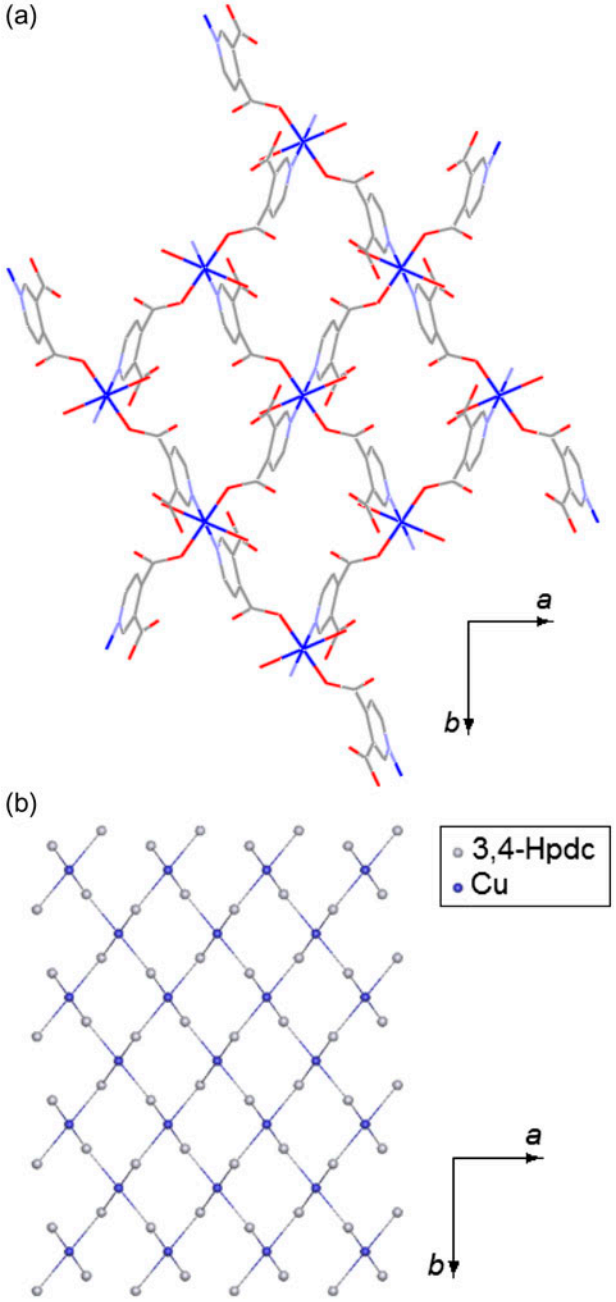

Figure 4. (a) View of the 2-D network of **1** along the crystallographic *c* axis. Hydrogens and lattice dmso molecules are omitted for clarity. (b) The simplified 2-D network for **1**, provided by TOPOs program package [51], showing the four-connected uninodal net of (*4*,*4*) topology.

In addition, PXRD patterns were recorded for **1** and **2** (figure 2), and they are comparable to the corresponding simulated patterns calculated from the single-crystal diffraction data, indicating phase purity of each bulk sample.

3.2. *Crystal structures*

Single-crystal X-ray diffraction analysis shows that both **1** and **2** crystallized in the monoclinic system with $P2_1/n$ and $P2_1/c$ space groups, respectively. As shown in figure 3, the metal center in both compounds is coordinated through two N and two O from two 3,4-Hpdc$^-$ ligands and two waters, resulting in six coordination with an octahedral geometry. Each 3,4-Hpdc$^-$ is partially deprotonated, with only one carboxylate involved in coordination toward the metal center in a monodentate mode, as suggested by infrared spectra. In **1**, the Cu–O5 bond distance (2.467(3) Å) is much longer than the Cu–O4 (1.977(2) Å) and Cu–N1^{ii} (2.006(2) Å) bond distances, characterizing a Jahn–Teller

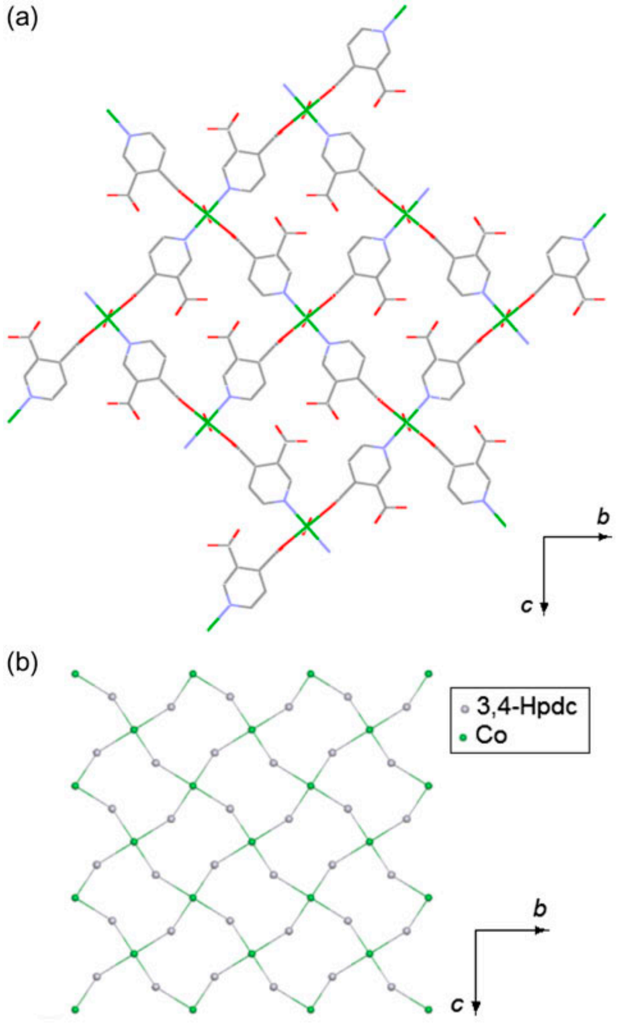

Figure 5. (a) View of the 2-D array of **2** along the crystallographic *a* axis. Hydrogens and lattice dmso and water molecules are omitted for clarity. (b) The simplified 2-D network of **2**, provided by TOPOs program package [51], showing the four-connected uninodal net of (*4*,*4*) topology.

distortion, while in **2,** all Co–O and Co–N bond distances are similar (2.094(2)–2.166(2) Å). All M–O and M–N distances are in accord with corresponding distances reported in the literature for similar compounds [13, 27].

In both **1** and **2**, the Cu(II) and Co(II) centers are linked by 3,4-Hpdc$^-$ ligands giving 2-D sheets in which the Cu···Cu distance is 8.781 Å and the Co···Co distance is 9.254 Å. These sheets can be classified as four-connected uninodal 2-D nets of (*4*,*4*) topology (figures 4 and 5) [51].

In **1,** there are two OH···O hydrogen bonds involving coordinated waters, one with the dmso molecules present in the network (d(O5···O6) = 2.906(4) Å, θ(O5–H5A···O6) = 148.9°) and one with the carboxylate (d(O5···O3^{i}) = 2.744(4) Å, θ(O5–H5B···O3) = 150.3°). In addition, the dmso is involved in another hydrogen bond with the carboxylic acid (d(O1···O6^{v}) = 2.590(3) Å, θ(O1–H1···O6^{v}) = 166.6°). All these hydrogen bonds, according to their geometrical parameters, can be classified as moderate [52–55]. Also, a weak CH···O hydrogen bond between the dmso methyl and O from carboxylate (d(C9^{v}···O3) = 3.512(6) Å, θ(C9^{vi}–H9A···O3) = 149.6°) can be observed. Despite the weakness of this interaction, it is probably key for the 3-D supramolecular packing. The difference between the overall structures of **1** and **2** is the presence of lattice water molecules in **2**. For **2**, there are cooperative, moderate OH···O hydrogen bonds between the coordinated water of one sheet and the lattice water (d(O5···O7) = 2.727(4) Å, θ(O5–H5A···O7) 174.64°) and between the lattice water molecule and the noncoordinated O of the carboxylate in the adjacent sheet (d(O7···O3^{v}) = 2.786(4) Å, θ(O7–H7B···O3^{v}) 161.81°), providing a

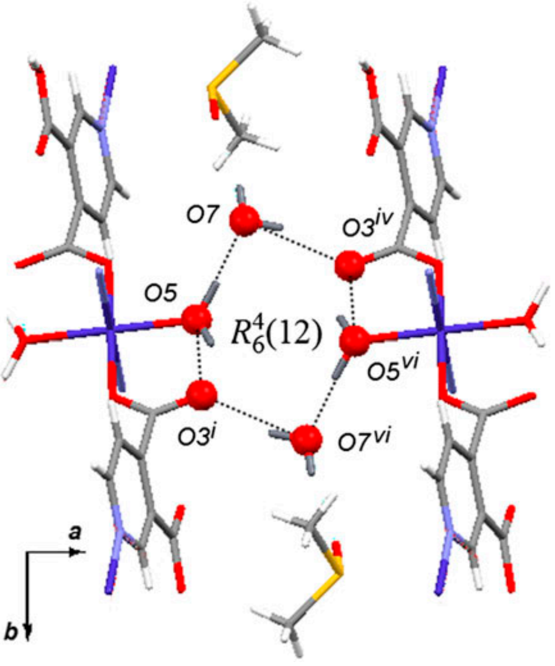

Figure 6. Hydrogen-bonding interactions in **2** between the coordinated water of one sheet and lattice water, and between the lattice water molecule and carboxylate of the adjacent sheet. Symmetry codes: *i* = 2 − *x*, −*y*, 2 − *z*; *iv* = 1 + *x*, *y*, *z*; *vi* = 3 − *x*, −*y*, 2 − *z*.

graph-set pattern $R_6^4(12)$ (figure 6). These hydrogen bonds promote the connection between 2-D sheets contributing to the 3-D supramolecular array. In addition, the O from dmso is involved in hydrogen bonds with the lattice water (d(O7···O6) = 2.815(4) Å, θ(O7–H7A···O6) 170.07°) and with the carboxylic acid (d($O1^{vi}$···O6) = 2.564(4) Å, θ ($O1^{vi}$H1···O6) = 167.49°).

The literature presents three papers describing coordination polymers formed by Cu(II) atoms and 3,4-pdc^{2-} anions [25–27]. The first presents $(NMe_4)_{2n}[Cu_3(\mu_{3-}3,4\text{-}pdc)_4(H_2O)_4]_n\cdot 4nH_2O$ (*vide supra*) [26], which has two crystallographic independent Cu(II) sites with square pyramidal and octahedral geometries, and the ligand is totally deprotonated, acting as a T-shaped connector and adopting the coordination mode (d) in chart 2. In the other two papers, the ancillary ligand 1,10-phenanthroline (phen) is present in the networks. In $[Cu(3,4\text{-}pdc)(phen)]\cdot H_2O$ [27], the Cu(II) centers are five coordinate, and the totally deprotonated 3,4-pdc^{2-} ligands adopt the same coordination mode as in $(NMe_4)_{2n}[Cu_3(\mu_{3-}3,4\text{-}pdc)_4(H_2O)_4]_n\cdot 4nH_2O$. The last paper describes the copper hydroxo complexes, $[Cu_4(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)(3,4\text{-}pdc)(phen)_4]_n\cdot n(3,4\text{-}pdc)\cdot 11.5nH_2O$, $[Cu_4(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(3,4\text{-}pdc)(phen)_4]_n\cdot n(3,4\text{-}pdc)\cdot 11.5nH_2O$, $[Cu_8(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_6(3,4\text{-}pdc)_2(phen)_8]\cdot 2(3,4\text{-}pdc)\cdot 23H_2O$, and $[Cu_{3.5}(\mu_2\text{-}OH)_3(3,4\text{-}pdc)_2(phen)]_n$ [14]. In the first two compounds, which are linkage isomers, all the Cu(II) centers are five coordinate, adopting a square-pyramidal geometry, and in the other two, there are four- and six-coordinate Cu(II) centers, in addition to five-coordinate centers. The coordination modes (a)–(e) in chart 2 were observed in this series of compounds. In all these examples, Cu(II) centers preferentially exhibit coordination number five in a square-pyramidal geometry, while in **1**, the Cu(II) centers are six coordinate in an octahedral geometry. Unlike all these examples, the 3,4-H_2pdc acid used in the synthesis of **1** is partially deprotonated (3,4-$Hpdc^-$), probably due to the synthesis conditions. In **1**, the 3,4-$Hpdc^-$ coordination mode is similar to (b) in chart 2, although the group in the 3-position is still a carboxylic acid.

The literature also reports coordination polymers constructed by Co(II) and 3,4-pdc^{2-} anions [13, 28, 29]. In all cases, hydro/solvothermal conditions and basic media were used in the syntheses, and as a result, the ligand was completely deprotonated, different from that in **2**. In one paper, $[Co(3,4\text{-}pdc)(H_2O)_2]_n\cdot nH_2O$ and $[Co_3(OH)_2(3,4\text{-}pdc)_2(H_2O)_2]_n$ were described, in which the 3,4-pdc^{2-} ligands adopt coordination modes (f) and (g) (chart 2), respectively [41]. As described in two other papers, the ancillary nitrogen-based ligands 1,2-bis(4-pyridyl)ethane (bpe) [13] and thiabendazole (TBZ) [29] were used in the syntheses, producing $\{[Co(3,4\text{-}pdc)(H_2O)(bpe)_{0.5}]\cdot 0.5H_2O\}_n$ and [Co(3,4-pdc)(TBZ)], in which coordination modes (f) and (h), respectively, were observed. In all these compounds, the Co (II) centers are six coordinate and adopt octahedral geometry, just like in **2**.

3.3. *EPR studies*

For investigation of the local symmetries and the existence of magnetic couplings between transition metal ions in **1** and **2**, EPR measurements were performed. The Cu^{2+} ion has $3d^9$ electronic configuration with one unpaired electron and $S = 1/2$, while the Co^{2+} ion ($3d^7$) has three unpaired electrons in a high-spin $S = 3/2$ configuration [56]. Both transition metal ions have naturally abundant isotopes with nuclear spins: ^{63}Cu, $I = 3/2$ (69%) and ^{65}Cu, $I = 3/2$ (31%), and ^{59}Co, $I = 7/2$ (100%). These give characteristic hyperfine splitting, resulting in 4-line (Cu) and 8-line (Co) hyperfine-split spectra. However, these hyperfine splittings are only observed for diluted samples and in the present case are hidden in the broad linewidths. The spin Hamiltonian describing the Cu^{2+} and Co^{2+} ions is usually written as:

$$H = \beta SgB + SDS + SAI \tag{1}$$

where the first term denotes the electron Zeeman interaction, the second denotes the electronic fine structure, and the third denotes the hyperfine interaction. The symbols have their usual meaning. Nuclear quadrupole interactions and nuclear Zeeman interactions can generally be neglected [56]. For calculation of EPR spectra of Cu(II), only the first and third terms of equation (1) have to be taken into account. For Co(II) in an octahedral

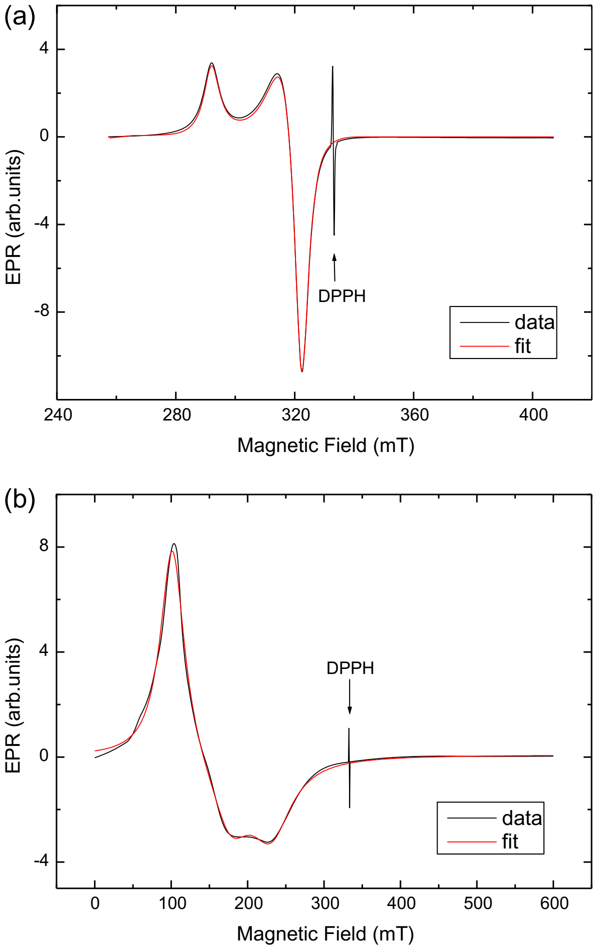

Figure 7. EPR spectra of polycrystalline samples of **1** (a) and **2** (b) measured with microwave frequency of 9.34 GHz at 300 K and 15 K, respectively. Measured spectra are shown in black together with the spin marker DPPH (*g* = 2.0037) and calculated spectra in red (see http://dx.doi.org/10.1080/00958972.2014.959002 for color version).

coordination, the zero-field splitting between the spin states is, in general, very large resulting in only one allowed spin transition between $m_s + 1/2 \rightarrow -1/2$, with highly anisotropic *g* values. In addition, the EPR spectra of Co(II) compounds have to be measured at low temperatures due to fast relaxation times.

Figure 7 shows the polycrystalline powder EPR spectra of **1** [figure 7(a)] and **2** [figure 7(b)], which were measured at 300 and 15 K, respectively, with a microwave frequency of 9.34 GHz. Both EPR spectra are described by broad, asymmetric EPR lines.

For simulation of the EPR spectra, only the electron Zeeman interaction, the first term of equation (1), has been used. The calculation of the EPR spectra is based on the exact diagonalization of the spin Hamiltonian. Gaussian lineshapes have been used to account for unresolved hyperfine interactions. The best simulations of the spectra are shown in figure 7 (red curves) and show good agreement with the experimental spectra (black curves).

The principal *g* tensor parameters for Cu(II) and Co(II) in **1** and **2** are g_1 = 2.29(1), g_2 = 2.10(1), g_3 = 2.07(1) and g_1 = 5.6(1), g_2 = 4.0(1), g_3 = 3.1(1), respectively. For both ions, the symmetry of the *g* tensors is consistent with rhombic or lower symmetries, as represented by the three independent *g* values. The average *g* values are 2.15(1) for Cu(II) and 4.2(1) for Co(II) in **1** and **2**, respectively. These average *g* values are expected for distorted octahedral symmetries for both transition metal ions. For both ions, the *g* values deviate considerably from those of the free electron due to a mixing of the orbital angular momentum of excited states into the ground states. The hyperfine interaction, although not resolved in the EPR spectra of both compounds, is also strongly asymmetric, which is manifested in the varying linewidths for the different principal directions of the *g* tensor. Magnetic coupling between nearest Cu and Co metal atoms was not observed, consistent with the X-ray structures of both compounds, where the metal–metal distances are large. The Cu···Cu distance for **1** within the 2-D sheets is 8.781 Å and between the sheets is 10.281 Å, while the corresponding Co···Co distances for **2** are 9.254 and 8.295 Å, respectively.

4. Conclusion

Two 2-D coordination polymers, $\{[Cu(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2dmso\}_n$ (**1**) and $\{[Co(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2H_2O\cdot 2dmso\}_n$ (**2**), were synthesized by the diffusion method. Both compounds contain the partially deprotonated species $3,4\text{-}Hpdc^-$. Many compounds synthesized from the parent acid and described in the literature were obtained in basic media under hydro/solvothermal conditions and present the totally deprotonated $3,4\text{-}pdc^{2-}$. Considering this fact, we can conclude that no base should be added to the reaction mixture, and mild reaction conditions should be used to obtain compounds containing the partially deprotonated $3,4\text{-}Hpdc^-$.

The thermal analysis results indicated that both compounds have coordinated water molecules and a dmso molecule in the network. Infrared spectra suggested that the starting acid H_2pdc was partially deprotonated and coordinated to the metal centers through one O from a carboxylate group in a monodentate fashion and one N from the pyridine ring. EPR spectra showed that the transition metal ions in both compounds adopted distorted octahedral symmetries without any magnetic coupling between metal sites. X-ray diffraction analyses confirm these results for both compounds. Additionally, the structural analysis revealed the polymeric nature of **1** and **2**, in which $3,4\text{-}Hpdc^-$ bridges the metal centers generating a four-connected uninodal 2-D net of (*4*,*4*) topology.

Supplementary material

IR spectra for **1** and **2**. Crystallographic data for $\{[Cu(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2dmso\}_n$ (**1**) and $\{[Co(3,4\text{-}Hpdc)_2(H_2O)_2]\cdot 2H_2O\cdot 2dmso\}_n$ (**2**) structures reported herein have been deposited at the Cambridge Crystallographic Data Center, CCDC 897986 and 897987. This information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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