

Facile adaptation of 1D Mn(II) chain motifs to form 3D azopyridine-based coordination polymers

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Abstract. We report the synthesis of a simple 1D Mn-azopyridine-based coordination polymer, *poly*-[Mn^{II}(NO₃)₂(OH₂)₂(azopy)]·2MeCN (**1**) (azopy = 4,4'-azobis(pyridine)) and its use as a convenient feedstock to afford two 3D coordination polymers, namely: *poly*-[Mn^{II}(azopy)₂(CNAgCN)₄] (**2**), and *poly*-[Mn^{II}₂(pda)(Hpda)₂(azopy)₂(OH₂)₂]·2MeCN (**3**), (pdaH₂ = 1,4-phenylenediacetic acid), respectively. The compounds have been characterised by elemental analysis, IR, PXRD, TGA and single crystal X-ray diffraction. Compound **1** is a 1D coordination polymer while **2** represents a 3-dimensional coordination polymer adopting 2-fold interpenetrated rutile (**rtl**) topology and **3** is a 5-connected 3-dimensional coordination polymer with boron nitride (**bnn**) topology.

Introduction

The design and synthesis of novel coordination polymers (CPs) continues to attract great attention because of their structural diversity and potential applications in areas such as catalysis,¹ gas separation and sorption,^{2,4} sensing,⁵ energy conversion,⁶⁻⁸ medicine,⁹ drug delivery¹⁰ and magnetism.¹¹

By carefully choosing metal nodes and organic linkers, desired materials such as one-, two- and three-dimensional (1D, 2D and 3D) compounds can be obtained and hence the structure design can be rationalised by the secondary building unit (SBU). While one-pot self-assembly has been successfully employed in the synthesis of a variety of such compounds, targeting specific materials through direct synthesis can be hindered due to limited linker solubility, chemical and/or thermal stability, or functional group incompatibility. Moreover, undesired reactions between linker functional groups and metal ions can lead to undesired products including amorphous materials, thus precluding the isolation of the desired materials in pure crystalline form.

The judicious choice of organic ligand, co-ligand, metal node

and/or metalloligand plays an important role in controlling the topology and dimensionality of the resulting coordination polymers and constitutes a promising strategy to construct high dimensional polymeric coordination structures.^{12,13} Along these lines, we recently reported discrete manganese coordination clusters some of which were successfully linked by nitrogen-based ligands to afford coordination polymers.¹⁴⁻¹⁶ Indeed, using appropriate metal-containing precursors can be a key factor to obtaining target materials.¹⁷

The need to prepare new coordination polymers as well as to create analogues of existing structures requires the development of new synthetic techniques to enrich the diversity and complexity of coordination polymers to achieve new functions.¹⁸ To this end, it has long been observed that various key factors, including the coordination geometry of the metal ions and the configuration and the binding mode of the organic ligands can frequently influence the self-assembly process¹⁹⁻²⁴ which is responsible for the variation in crystal packing and overall network superstructures.^{25,26}

Although metal coordination compounds and polymers based on conjugated bipyridine ligands such as 4,4'-azobis(pyridine) (azopy)^{27,28} have been intensively studied, their implication in the deliberate synthesis of coordination polymers and modulation thereof is an attractive perspective as the resulting materials could find application in the areas such as molecular switching.²⁹ Dicyanoargentate ion is a versatile bridging ligand that has application for constructing multidimensional polymers. It has been employed in the controlled preparation of mixed-metal

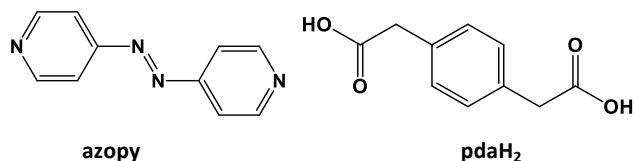
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(heterometallic) coordination polymers with pre-formed primary building units.³⁰ Dicarboxylate ligands in their part have been widely used in the synthesis of MOFs and coordination polymers. While most of the work has been carried out with rigid polycarboxylate ligands such as those derived from the 1,4-benzenedicarboxylate³¹ and functionalised tribenzoic acids,³²⁻³⁴ studies of complex formation between transition metal ions and more flexible 1,4-phenylenediacetic acid (pdaH₂) are not so common.³⁵ The target of this work is to obtain structurally related coordination polymers by exploiting the coordination flexibility of the metal node which can be modified by careful selection of the primary and secondary linkers.

Herein we present the synthesis and characterisation of three coordination polymers that are stabilised by azobis(pyridine) ligands, namely, *poly*-[Mn^{II}(NO₃)₂(OH₂)₂(azopy)]·2MeCN (**1**), *poly*-[Mn^{II}(azopy)₂(CNAgCN)₄] (**2**), and *poly*-[Mn^{II}₂(pda)(pdaH)₂(azopy)₂(OH₂)₂]·2MeCN (**3**) (azopy = 4,4'-azobis(pyridine) and pdaH₂ = 1,4-phenylenediacetic acid, Scheme 1). Compound **1** is a 1D coordination polymer while **2** and **3** represent 3D coordination polymers adopting 2-fold interpenetrated rutile (**rtl**) topology and a boron nitride (**bnn**) topology, respectively and are obtained by treating **1** with potassium dicyanoargentate (**2**) or 1,4-phenylenediacetic acid (**3**).



Scheme 1. Structures of azopy (4,4'-azobis(pyridine)) and pdaH₂ (1,4-phenylenediacetic acid)

Experimental

Materials and Methods

General: Unless otherwise stated all reagents were obtained from commercial sources, and were used as received, without further purification. The reactions were carried out under aerobic conditions. Elemental analyses (CHN) were performed at the School of Chemistry and Chemical Biology, University College Dublin, using Exeter Analytical CE 440 elemental analyser. FTIR spectra were measured on a Perkin Elmer Spectrum 100 FTIR/ATR. Thermal gravimetric analyses were performed in a nitrogen atmosphere in the temperature range 30-800 °C with a heating rate of 2 °C min⁻¹, using a Perkin Elmer Pyris 1 TGA. ~4–6 mg of dried material were used for the measurements. Powder X-ray Diffraction (PXRD) studies were carried out using a Bruker D2 Phaser diffractometer.

Synthesis:

***poly*-[Mn^{II}(NO₃)₂(OH₂)₂(azopy)]·2MeCN (**1**).** Mn(NO₃)₂·4H₂O (126 mg, 0.5 mmol) together with 4,4'-azopyridine (93 mg, 0.5 mmol) were dissolved in 20 mL of MeCN stirred at room temperature for 30 minutes then refluxed for 2h and filtered. Pink crystals of **1** were obtained within 2h. (yield: 110 mg, 45% based on azopyridine).

Elemental analysis (%) calculated (found): C 34.94 (34.98), H 3.77 (3.64), N 23.28 (23.34). IR (cm⁻¹) 3237 (br, m), 1625 (s), 1448 (s), 1289 (m), 1064 (vs), 1017(s), 987 (m), 837 (vs), 825 (vs), 716 (m).

***poly*-[Mn^{II}(azopy)₂(CNAgCN)₄] (**2**).** Complex **1** (96 mg, 0.2 mmol) together with KAg(CN)₂ (100 mg, 0.5 mmol) were dissolved in 20 mL of MeOH stirred at room temperature for 30 minutes then refluxed for 4h and filtered. Brown crystals of **2** were obtained after three weeks. (yield: 35 mg, 24 % based on **1**). Elemental analysis (%) calculated (found): C 38.79 (38.98), H 2.17 (2.24), N 22.62 (22.56). IR, (cm⁻¹) 3400 (br, m), 3303 (m), 2142 (s), 2080 (s) 1598 (s), 1535 (s), 1410 (m), 1049 (s), 838 (vs).

***poly*-[Mn^{II}₂(pda)(Hpda)₂(azopy)₂(OH₂)₂]·2MeCN (**3**).** **Method 1:** Complex **1** (96 mg, 0.2 mmol) together with 1,4-phenylenediacetic acid (136 mg, 0.7 mmol) were dissolved in 20 mL of MeOH/MeCN (2:1) stirred at room temperature for 30 minutes then refluxed for 4h and filtered. Yellowish brown crystals of **3** were obtained after five days. (yield: 30 mg, 26 %, based on **1**). Elemental analysis (%) calculated (found): C 55.20 (55.36), H 4.46 (4.65), N 11.92 (11.84). IR, (cm⁻¹) 3246 (br, m), 1714 (s), 1598 (s), 1542 (vs), 1381 (vs), 1244(s), (1139 (m), 1048 (w), 1012 (m), 838 (vs). **Method 2:** To a stirred slurry of azopyridine (93 mg, 0.5 mmol) and Mn(NO₃)₂·4H₂O (126 mg, 0.5 mmol) in MeOH/MeCN (2:1, 20 ml) was added in small portions, solid 1,4-phenylenediacetic acid (136 mg, 0.7 mmol). The resulting mixture was further stirred for 30 mins then refluxed for 4h, cooled and filtered. The filtrate was allowed to evaporate slowly to afford crystals of **3** after ten days. Yield (12 %). The compound was identified by unit cell indexation.

X-ray Crystallography

Structural and refinement parameters are presented in Table 1. All diffraction data were collected using a Bruker APEX-II Duo dual-source instrument using graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. Datasets were collected using ω and ϕ scans with the samples immersed in oil and maintained at a constant temperature of 100 K using a Cobra cryostream. The data were reduced and processed using the Bruker APEX suite of programs.³⁶ Multi-scan absorption corrections were applied using SADABS.³⁷ The diffraction data were solved using SHELXT and refined by full-matrix least squares procedures using SHELXL-2015.³⁸⁻⁴⁰ The functions minimized were $\sum w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were placed in calculated positions and refined with a riding model, with isotropic displacement parameters equal to either 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. Where appropriate, the positions of hydrogen atoms involved in hydrogen bonding interactions were refined to provide the best fit for the residual Fourier peaks and assigned a U_{iso} value equal to 1.5 times that of the nearest associated atom, with the

Table 1. Crystallographic Data for **1-3**.

formula	C ₁₄ H ₁₈ MnN ₈ O ₈ (1)	C ₂₄ H ₁₆ Ag ₂ MnN ₁₂ (2)	C ₂₇ H ₂₆ MnN ₅ O ₇ (3)
Mr, [g mol ⁻¹]	481.30	743.17	587.47
crystal system	Orthorhombic	monoclinic	monoclinic
space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
T [K]	100(2)	100(2)	100(2)
a [Å]	7.4909(2)	9.1567(4)	13.4938(4)
b [Å]	11.8073(4)	10.5450(5)	8.7231(3)
c [Å]	24.3162(8)	14.0966(6)	22.5819(6)
V [Å ³]	2150.70(12)	1349.24(10)	2646.42(14)
Z	4	2	4
ρ _{calcd} [g/cm ⁻³]	1.486	1.829	1.474
λ [Å]	0.71073	0.71073	0.71073
μ [mm ⁻¹]	0.671	1.936	0.555
<i>F</i> (000)	988	726	1216
reflections collected	84852	21852	205219
unique data	5827	3498	11063
<i>R</i> _{int}	0.0339	0.0151	0.0323
data with <i>I</i> > 2σ(<i>I</i>)	5827	3498	11063
parameters/restraints	294/7	178/0	401/3
<i>S</i> on <i>F</i> ² (all data)	1.097	1.058	1.052
w <i>R</i> ₂ (all data)	0.1133	0.0344	0.0846
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0452	0.0135	0.0312
largest residuals [e Å ⁻³]	+1.588/-0.852	+0.803 and -0.235	+0.509 and -0.348
CCDC	1504853	1504854	1504855

appreciation that the exact positions of these atoms cannot be meaningfully inferred from X-ray diffraction data.

Results and Discussion

Structure of poly-[Mn^{II}(NO₃)₂(OH₂)₂(azopy)]·2MeCN (**1**)

Single crystals of compound **1** were obtained by the reaction of 4,4'-azobis(pyridine) with manganese nitrate in MeCN under reflux conditions. The crystals of **1** were analysed by single-crystal X-ray diffraction, and the diffraction data were solved and refined in the orthorhombic space group *Pna*2₁. The asymmetric unit of **1** contains one manganese(II) ion, and one molecule of azopy coordinating to two equivalent metal ions through the pyridyl nitrogen atoms, shown in Fig. 1. The octahedral coordination sphere of the metal ion is completed by two unique nitrate ligands and two aqua

ligands, and two unique lattice acetonitrile molecules are also present within the asymmetric unit. The metal ion adopts a distorted octahedral geometry with all bond lengths varying in the range between 2.149(3) and 2.272(4) Å, with the pyridyl groups at the larger end giving an octahedral distortion parameter Σ = 65°.⁴¹ Extension of the structure through the bridging azopy ligands gives rise to a 1-dimensional coordination polymer.

Intermolecular interactions in the structure of **1** are dominated by hydrogen bonding involving the four aqua ligands and the nitrate ligands of adjacent strands (Fig. 2). These interactions can be described with two distinct graph sets: A series of corner-shared *R*₂²(12) cyclic motifs, each linking two adjacent metal centres. These loops are edge-shared with ribbons consisting of *R*₂²(10) loops which each link three chains. The tiling of these cyclic motifs defines a 2-dimensional hydrogen-bonded layer which extends parallel to

the *bc*-plane, and which is linked by azopy groups into an overall three-dimensional structure. The criss-crossed coordination linkages between the 2-dimensional hydrogen bonded layers leaves 1-dimensional solvent-filled channels in the structure which contain well-ordered lattice acetonitrile molecules. The structural details of hydrogen bonding for **1** are given in Table S1. Although adjacent azopy molecules are oriented parallel to one-another, the inter-planar distance between each group of 3.74 Å precludes the assignment of any substantial π - π interaction to this packing motif.

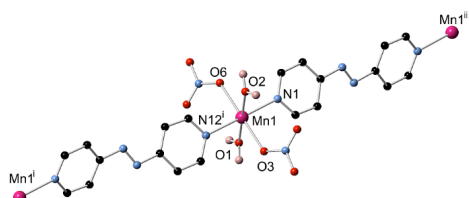


Fig. 1 Metal environment in compound **1** with partial atom labelling scheme. Carbon-bound hydrogen atoms are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$

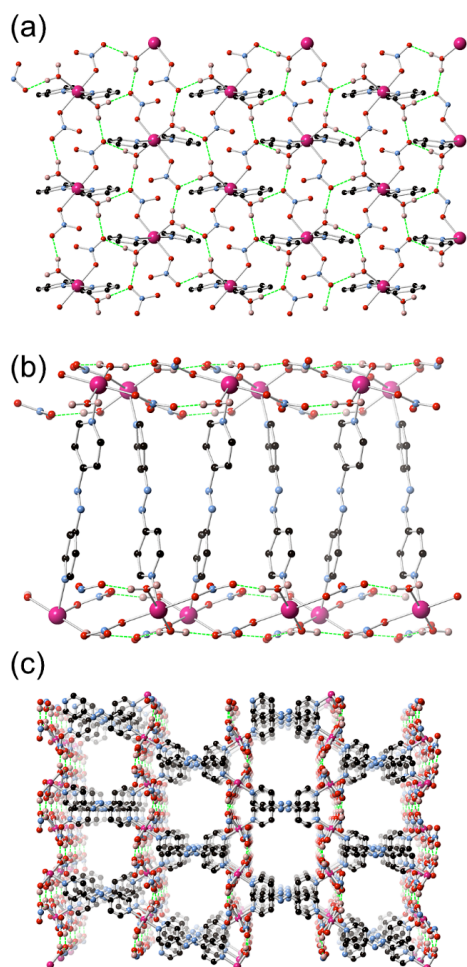


Fig. 2 (a) Structure of the hydrogen-bonded sheet involving the aqua and nitrate ligands in the structure of **1**; (b) Linkages between the hydrogen-bonded layers by **azopy** ligands in **1**; (c) Extended structure of **1** showing the primary solvent channels. Hydrogen atoms and acetonitrile molecules are omitted for clarity.

Use of compound **1** as a precursor

Given that compound **1** was obtained in appreciable yield and considering that it contains labile aqua ligands and unidentate nitrate ligands at the metal centre, we considered this material as starting material in further reactivity studies. Hence, treating a solution prepared from **1** with potassium dicyanoargentate or 1,4-phenylenediacetic acid (pdaH₂) afforded the coordination polymers $\{[(\text{Mn}^{\text{II}}(\text{azopy})_2(\text{CNAgCN})_4)]\}$ (**2**), and $\{\text{Mn}^{\text{II}}_2(\text{pda})(\text{Hpda})_2(\text{azopy})_2(\text{OH}_2)_2\} \cdot 2\text{MeCN}$ (**3**), respectively. Dicyanoargentate was selected because it is a versatile bridging ligand that can be employed to construct multidimensional coordination polymers,³⁰ while pdaH₂ was chosen because of the intrinsic flexibility provided by the central *bis*-benzyl moiety.

Structure of $\text{poly}\{[\text{Mn}^{\text{II}}(\text{azopy})_2(\text{CNAgCN})_4]\}$ (**2**)

Single crystals of **2** were analysed by single crystal X-ray diffraction, and the diffraction data were solved and refined in the monoclinic space group $P2_1/n$. The asymmetric unit of **2** contains one manganese(II) ion occupying a crystallographic special position, one **azopy** ligand, one silver(I) ion and two associated cyanido ligands. Each cyanido ligand bridges between the silver and manganese ions, coordinating *via* the carbon atom to the silver ion and through the nitrogen atom to the manganese ion. The **azopy** ligand also coordinates to both the manganese ion and the silver ion through the two pyridine nitrogen atoms. The silver ion adopts a T-shaped, 3-coordinate geometry (Fig. 3a), with the two cyanido ligands approximately co-axial (C17-Ag1-C16 angle 161.12(5)°), at Ag-C distances of 2.0867(13) and 2.0879(13) for C17 and C16, respectively. The **azopy** nitrogen atom is weakly coordinated at a greater distance of 2.5080(11). The manganese ion displays an octahedral coordination geometry ($\Sigma = 26^\circ$) and is coordinated by four nitrogen atoms from cyanido ligands, and two equivalent **azopy** nitrogen atoms in a *trans* arrangement, shown in Fig. 3b. The **azopy** nitrogen atoms coordinate at a slightly greater distance of 2.3046(9) Å, compared to the cyanido nitrogen atoms at N-Mn distances of 2.1999(12) and 2.2347(11) Å for N15 and N18, respectively.

The extended structure of **2** is a three-dimensional coordination polymer consisting of three-connected (Ag) and six-connected (Mn) nodes linked by two types of linear bridging ligand. The network adopts a rutile (*rtl*) topology common for binodal 3,6-connected nets, shown in Fig. 4. By virtue of the relatively large bridging distances between the nodes, twofold interpenetration is also observed in the structure. The two interlocked nets interact with one another through weak interactions between the azo nitrogen atoms of the **azopy** and the vacant coordination sites of the silver ion from the adjacent network, with Ag-N contact distances of 3.2548(11) and 3.1981(11) Å for the two interactions originating from nitrogen atom N7. Due to the close packing of the interpenetrated nets, no substantial void space or encapsulated solvent molecules are observed in the structure of **2**.

It should be pointed here that compound **2** could only be obtained by using compound **1** as feedstock, and could not be

prepared by direct synthesis from the respective components under identical reaction conditions. While the structure of **2** is not directly related to that of **1**, we speculate that compound **1** serves a source azopy and Mn²⁺ which reassembles in the presence of KAg(CN)₂ to afford compound **2**.

Structure of *poly*-[Mn^{II}₂(pda)(Hpda)₂(azopy)₂(OH₂)₂·2MeCN (**3**)

Single crystals of **3** were analysed by single crystal X-ray diffraction, and the diffraction data were solved and refined in the monoclinic space group *P*2₁/*n*. The asymmetric unit of **3** contains one manganese ion and an associated aqua ligand, one molecule of a singly protonated **Hpda**, half a fully deprotonated **pda** ligand, an **azopy** ligand and one lattice acetonitrile molecule. The manganese ion is coordinated in an {N₂O₄} octahedral geometry ($\Sigma = 38^\circ$) by three carboxylate oxygen atoms, one aqua ligand and two **azopy** pyridine nitrogen atoms.

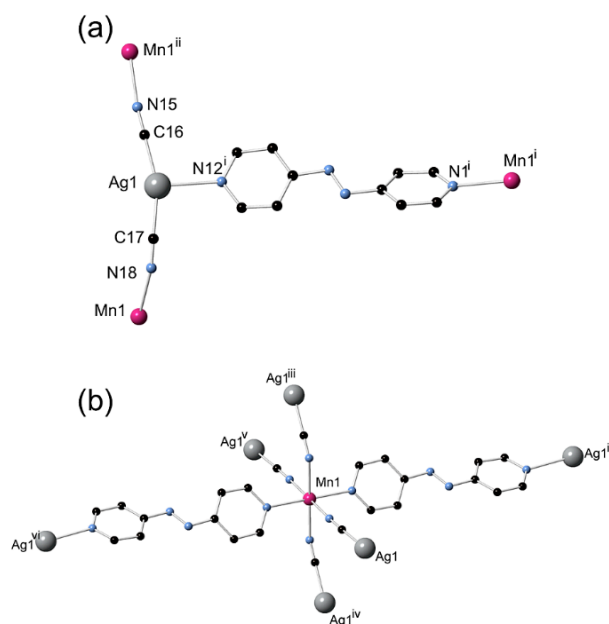
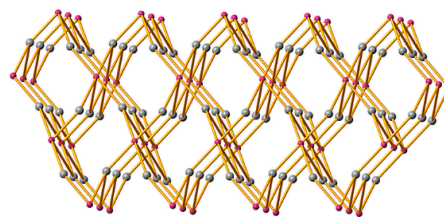


Fig. 3 Metal site environment in the structure of **2**, showing (a) the silver coordination sphere and (b) the manganese coordination sphere, with partial atom labelling scheme. Hydrogen atoms are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) 1-x, 1-y, 1-z; (ii) ½-x, ½+y, ½-z; (iii) ½+x, 3/2-y, z-½; (iv) -½-x, y-½; (v) -x, 1-y, -z; x-1, +y, z-1.

Each of the three crystallographically unique bridging ligands connects two manganese ions; the **azopy** and **pda** ligands each provide monodentate coordination at each binding site, while the **Hpda** ligand bridges two manganese ions in a μ_2 -κO:κO' coordination mode involving a single carboxylate group. The carboxylic acid functionality of this molecule, disordered over two related orientations in a 90:10 ratio, engages in a hydrogen bonding interaction with the non-coordinating carboxylate oxygen atom O6 of a nearby **pda** ligand. The Mn-N distances for coordination through the **azopy** ligand are comparable to those observed in structures **1** and **2**, at

(a)



(b)

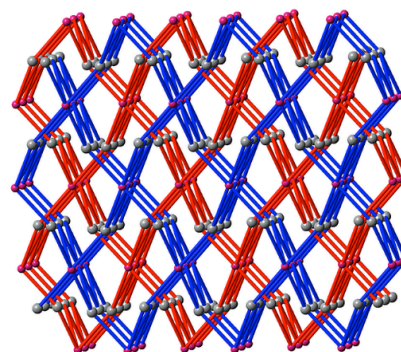


Fig. 4 Topological representation of the extended structure of **2**; (a) an individual rtl net, with manganese nodes coloured purple and silver nodes coloured grey, and all links coloured orange; (b) the interpenetrated structure of **2** with independent networks coloured separately.

2.2789(9) and 2.2747(9) Å for N1 and N12, respectively. The Mn-O distances fall in the range 2.1511(6) – 2.1725(8) Å for carboxylate coordination, and 2.1627(7) Å for coordination by O7 of the aqua ligand. Outer sphere hydrogen bonding is present between the aqua ligand O7 and two nearby carboxylate oxygen atoms (Table S1). The non-coordinating oxygen atom O6 from a carboxylate moiety acts as a hydrogen bond acceptor to give an $R_1^1(6)$ loop including one metal ion, and the coordinating oxygen atom O1 involved in the μ_2 -κO:κO' bridging of the **Hpda** ligand accepts a hydrogen bond from the aqua ligand resulting in an $R_1^1(8)$ loop containing two metal ions.

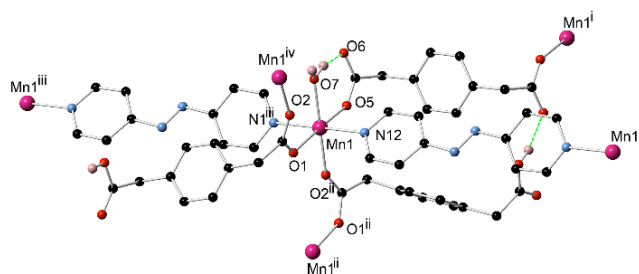


Figure 5 Coordination environment of the manganese ion in the structure of **3** with partial atom labelling scheme. Selected hydrogen atoms, and solvent molecules are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) 1-x, 1-y, 1-z; (ii) 3/2-x, ½+y, ½-z; (iii) 1+x, +y, +z; (iv) 3/2-x, y-½, ½-z; (v) x-1, +y, +z.

The extended structure of **3** is a three-dimensional polymeric network consisting of five-connected manganese nodes linked by three types of two-connected ligands. The topology is equivalent to the (4⁶.6⁴) **bnn** (boron nitride) structure. The mis-match between bridging distances (13.4938(4), 11.5085(8) and 5.2126(5) Å for **azopy**, **pda** and **Hpda**, respectively) leads to some degree of distortion from the idealised geometry. The lattice acetonitrile molecules align into narrow, one-dimensional solvent channels extending parallel to the crystallographic *b*-axis, while the flexible nature of the **Hpda/pda** ligands leads to efficient packing of the remainder of the structure. No additional void volume or solvent molecules were located within the structure.

It is noteworthy that compound **3** could also be obtained directly from the reaction of azopy and pdaH₂ with manganese nitrate. However, the yield through this route was considerably lower (12 %) than when the compound **1** was employed as feedstock. The identity of the product was established by unit cell indexing. Hence, whilst at first sight the synthetic strategy employing compound **1** as source of Mn²⁺ and azopy might appear rather unnecessary it proves to be a means of obtaining compound **3** in a higher yield.

Compounds **1-3** share the commonality of azobis(pyridine) moieties bonded to Mn²⁺ ion and differ in the coordination environment at this centre. In compound **2** the two H₂O and two NO₃ ligands have been replaced by four CNAgCN ligands (Fig. 3) while in **3** one H₂O ligand and two NO₃ ligands have been replaced by three carboxylate oxygen atoms from three **pda** ligands (Fig. 5). In overall, the three compounds are derived from a mixed-ligand-based strategy targeted at the development of three related yet distinct coordination polymers.

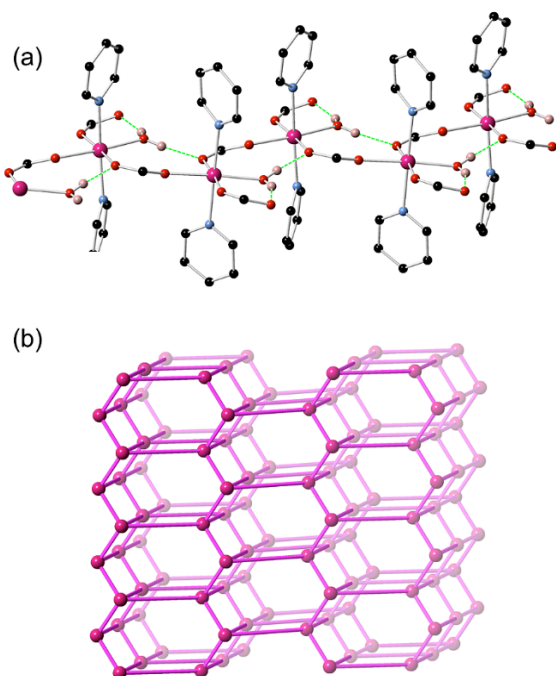


Fig. 6 (a) The hydrogen bonding interactions between the aqua and carboxylate ligands within the structure of **3**. Selected backbone and hydrogen atoms are omitted for clarity. (b) Topological representation of the **bnn** network adopted by **3**, with five-connected nodes representing manganese ions and bridging ligands simplified to links.

Thermogravimetric and PXRD analysis

The thermal behaviour of compounds **1-3** was analysed by thermogravimetric analysis (TGA) measurements under nitrogen (Fig. S1). The TGA curve of **1** revealed an initial weight loss of 16 % upon heating to 110 °C, followed by a two-step weight loss of about 23% (15 % + 8 %) at 160 °C, which in overall corresponds to the loss of two interstitial acetonitrile molecules and the two coordinated waters ligands, respectively. The compound decomposes to an unidentified product(s) above 250 °C. TGA analysis of **2** and **3** revealed that the compounds are stable up to 110 and 450 °C, respectively, decomposing thereafter to unidentified products above these temperatures. The plot for **3** did not plateau even at 800 °C.

Building chemical structures from multiple ligands and metallic centres or different metals is an outstanding challenge because of phase separation and the increasing number of possible outcomes. The phase-purity of the bulk materials was analysed by powder X-ray diffraction (PXRD). The PXRD profiles of as synthesised compounds **1-3** (Figs. S2 - S4) matched the simulated, based on the single-crystal X-ray structure. These experiments, combined with elemental analyses and IR spectra confirm that the crystalline materials are pure phases.

Conclusions

We have reported the synthesis of a 1D Mn-azopyridine-based coordination polymer, *poly*-[Mn^{II}(NO₃)₂(OH₂)₂(azopy)]·2MeCN (**1**) which has been exploited as a convenient starting material to access the 3D coordination polymers *poly*-[Mn^{II}(azopy)₂(CNAgCN)₄] (**2**) and *poly*-[Mn^{II}₂(pda)(Hpda)₂(azopy)₂(OH₂)₂]·2MeCN (**3**). The method demonstrated opens a route to obtaining desired materials with potential functionalities. Indeed, compound **3** lends itself to further elaboration through post-synthetic metalation to introduce metal complexes to the vacant coordination sites of the CO₂H/CO₂ moieties. Such elaboration is very important in further developing new synthetic strategies.

Acknowledgements

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Graphical Abstract:

