

Synthesis, structures and magnetic properties of two 3D 3,4-pyridinedicarboxylate bridged manganese(II) coordination polymers incorporating 1D helical Mn(carboxylate)₂ chain or Mn₃(OH)₂ chain

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Abstract

The hydrothermal reactions of MnCl₂·4H₂O, 3,4-pyridinedicarboxylic acid (3,4-pydaH₂) and triethylamine in aqueous medium yield two 3D metal–organic hybrid materials, [Mn(3,4-pyda)] (1) and [Mn₃(OH)₂(3,4-pyda)₂(H₂O)₂] (2), respectively. In both complexes, each 3,4-pyda acts as a pentadentate ligand to connect five Mn(II) atoms via the pyridyl group and the two μ₂-carboxylate groups (one in *syn,anti*-mode and one in *syn-syn* mode for 1 and both in *syn,anti*-mode for 2). Complex 1 possesses an interesting 3D coordination polymeric structure incorporating 1D helical Mn(μ₂-carboxylate)₂ chain units, in which each Mn(II) atom is coordinated in less common square pyramidal geometry to four carboxylate oxygen atoms and one pyridyl nitrogen atom. Each 3,4-pyda links three helical Mn(μ₂-carboxylate)₂ chains and each Mn(μ₂-carboxylate)₂ chain is linked by other eight helical Mn(μ₂-carboxylate)₂ chains via sharing 3,4-pyda bridges. Complex 2 is a 3D coordination network consisting of 1D Mn₃(OH)₂ chains and 3,4-pyda bridges. The repeating trimeric structural unit in the manganese(II) hydroxide chain consists of two edge-sharing symmetry-related manganese octahedra linked via μ₃-OH to a vertex of Mn₂ octahedron. Each 3,4-pyda links three Mn₃(OH)₂ chains and each Mn₃(OH)₂ chain is linked by other six Mn₃(OH)₂ chains via 3,4-pyda bridges, resulting in a 3D coordination solid. Magnetic measurements reveal that a weak antiferromagnetic interaction between the Mn^{II} ions occurs in complex 1 and a 3D magnetic ordering at about 7.0 K in complex 2.

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1. Introductions

The rapidly expanding field of solid engineering of 2D and 3D coordinated polymers is of great current interest for both the structural and topological novelty of such organic–inorganic frameworks, as well as for their potential applications to material science as catalytic, conductive, luminescent, magnetic, nonlinear optical or porous materials [1–4]. The main strategy popularly used in this area is a building-block approach [5]. Several metal ions may also be aggregated into larger units by appropriate multidentate connectors to act as secondary building units for the overall framework [6].

The versatility of organic functional groups (such as 4,4'-bipyridine and its analogues, polycarboxylates, pyridinecarboxylates) and the diversity of metal-hydroxide units have led to a wide array of functional organic–inorganic hybrid materials [7–9]. Pyridine-*n,m*-dicarboxylic acid (*n,m*-pyda, *n,m* = 2–5) seems to be an excellent building block with charge and multiconnecting ability, that has not, to our knowledge, been well documented as the connector in the design of functional coordination polymers [7e,10–12]. Of particular interest to us is the exploration of function-structural correlations in the transition metal compounds of *n,m*-pyda (*n,m* = 2–4) with theoretically important topologies. In a recent communication we reported two interesting cobalt(II) coordination polymers of 3,4-pyda, one is a 2D coordination bilayered polymer, and the other is 3D

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coordination polymer with inorganic $\text{Co}_3(\text{OH})_2$ chains [12a]. In our continuing investigation on this interesting system, we report here synthesis, crystal structures and magnetic properties of two 3D 3,4-pyda-bridged manganese(II) co-ordination networks: $[\text{Mn}(3,4\text{-pyda})]$ (**1**) and $[\text{Mn}_3(\text{OH})_2(3,4\text{-pyda})_2(\text{H}_2\text{O})_2]$ (**2**).

2. Experimental section

All reagents were used as received from commercial sources, and water was distilled before use. The C, H, N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range $400\text{--}4000\text{ cm}^{-1}$ on a Perkin-Elmer 2000 FTIR spectrophotometer. Magnetic susceptibility $\chi_M(T)$ and magnetization $M(H)$ measurements on polycrystalline samples were performed using a Quantum Design SQUID magnetometer. In $\chi(T)$ measurements, the temperature was varied from 2 to 300 K. Magnetic fields of 5 and 10 kOe were applied in $\chi_M(T)$ measurements. $M(H)$ was measured from 0 to 50 kOe at 2 K. Experimental magnetic susceptibility data were corrected from diamagnetism of the constituent atoms [13]. The effective molar magnetic moments were calculated with the equation $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$.

2.1. Synthesis of $[\text{Mn}(3,4\text{-pyda})]$ (**1**)

An aqueous mixture containing $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.197 g, 1.0 mmol), 3,4-pydaH₂ (0.167 g, 1.0 mmol), NEt_3 (0.202 g, 2.0 mmol) and water (10 cm³, 555.5 mmol) was placed in a Parr Teflon-lined stainless steel vessel (23 cm³). The pH value of the starting reaction system is ca. 9. The vessel was sealed and heated to 175 °C for 24 h and then cooled to 100 °C at a rate of 5 °C/h, and held for another 10 h, followed by further cooled to room temperature. Colorless polyhedral crystals of **1** were collected, washed with water and dried in air (yield 70%). The pH value of the final reaction system is ca. 7. Anal. Calc. for $\text{C}_7\text{H}_3\text{MnNO}_4$: C, 38.21; H, 1.37; N, 6.37%. Found: C, 37.95; H, 1.23; N, 6.18%. IR (KBr, cm⁻¹): 3051_w, 1621_{vs}, 1596_s, 1395_{vs}, 1297_w, 1171_w, 1126_w, 1071_w, 986_w, 904_w, 855_m, 821_m, 793_w, 733_m, 609_m, 532_w, 473_m.

2.2. Synthesis of $[\text{Mn}_3(\text{OH})_2(3,4\text{-pyda})_2(\text{H}_2\text{O})_2]$ (**2**)

An aqueous mixture containing $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.297 g, 1.5 mmol), 3,4-pydaH₂ (0.167 g, 1.0 mmol) and Et_3N (0.303 g, 3.0 mmol) and water (10 cm³, 555.5 mmol) was placed in a Parr Teflon-lined stainless steel vessel (23 cm³). The pH value of the starting reaction system is >12. The vessel was sealed and heated to 180 °C for 72 h and then cooled to room temperature at a rate of 5 °C/h, Pale yellow

Table 1
Crystal data and structure refinement for **1** and **2**

	1	2
Formula	$\text{C}_7\text{H}_3\text{MnNO}_4$	$\text{C}_{14}\text{H}_{12}\text{Mn}_3\text{N}_2\text{O}_{12}$
Fw	220.04	565.08
Crystal system	Orthorhombic	Triclinic
Space group	$Pca2_1$	$P-1$
$a/\text{Å}$	14.737(3)	6.6293(7)
$b/\text{Å}$	6.026(2)	6.9794(7)
$c/\text{Å}$	7.261(2)	10.359(1)
$\alpha/^\circ$		75.259(2)
$\beta/^\circ$		71.010(2)
$\gamma/^\circ$		75.764(2)
$V/\text{Å}^3$	644.9(3)	431.3(1)
Z	4	1
$D_c/\text{g cm}^{-3}$	2.267	2.176
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	2.017	2.239
No. unique data	1922	1717
No. data with $I > 2\sigma(I)$	1047	1564
R_1, wR_2^a	0.0343, 0.0819	0.0319, 0.0815

$$^a R_1 = \frac{\sum \|F_o| - |F_c|\|}{\sum |F_o|}, \quad wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}, \quad w = \left[\sigma^2(F_o)^2 + (0.1(\max(0, F_o^2) + 2F_c^2)/3)^2 \right]^{-1}.$$

crystals of **2** were separated from another brown solid phase (ca. 45% yield). The pH value of the final reaction system is ca. 6. Anal. Calc. for $\text{C}_{14}\text{H}_{12}\text{Mn}_3\text{N}_2\text{O}_{12}$: C, 29.76; H, 2.14; N, 4.96%. Found: C, 29.52; H, 2.06; N, 4.58%.

2.3. X-ray crystallography

Diffraction intensities for **1** and **2** were collected at 20 °C on a Bruker Smart Apex CCD diffractometer (Mo $K\alpha$, $\lambda = 0.71073\text{ Å}$). Absorption corrections were applied by using SADABS [14]. The structures were solved with direct methods and refined with full-matrix least-squares technique using the SHELXLTL program package [15]. Anisotropic displacement parameters were applied to all nonhydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic displacement parameters. The Flack parameter is 0.05(4) for complex **1**. The crystallographic data for **1** and **2** are listed in Table 1. Selected interatomic contacts (Å) and bond angles (°) for **1** and **2** are given in Table 2.

3. Results and discussion

3.1. Syntheses and characterization

Recently, hydrothermal method has been effectively used for the syntheses of crystalline coordination polymers. It has been found that some changes of

Table 2
Selected interatomic contacts (Å) and bond angles (deg) for **1** and **2**

Complex 1			
Mn(1)–O(1a)	2.138(3)	Mn(1)–O(4d)	2.159(3)
Mn(1)–O(3b)	2.141(3)	Mn(1)–N(1)	2.225(4)
Mn(1)–O(2c)	2.143(3)		
O(1a)–Mn(1)–O(3b)	84.3(1)	O(2c)–Mn(1)–O(4d)	86.6(1)
O(1a)–Mn(1)–O(2c)	91.4(1)	O(1a)–Mn(1)–N(1)	168.4(1)
O(3b)–Mn(1)–O(2c)	96.4(1)	O(3b)–Mn(1)–N(1)	91.5(1)
O(1a)–Mn(1)–O(4d)	91.4(1)	O(2c)–Mn(1)–N(1)	99.8(1)
O(3b)–Mn(1)–O(4d)	174.8(1)	O(4d)–Mn(1)–N(1)	92.1(1)
Complex 2			
Mn(1)–O(1b)	2.157(2)	Mn(1)–O(2)	2.245(2)
Mn(1)–O(1)	2.186(2)	Mn(2)–O(1)	2.191(2)
Mn(1)–O(5a)	2.154(2)	Mn(2)–O(3)	2.233(2)
Mn(1)–O(1w)	2.204(2)	Mn(2)–O(4a)	2.2484(2)
Mn(1)–N(1c)	2.285(2)	Mn(1)···Mn(1b)	3.128(1)
O(5a)–Mn(1)–O(1b)	175.81(7)	O(1)–Mn(1)–N(1c)	168.92(8)
O(5a)–Mn(1)–O(1)	91.28(7)	O(1w)–Mn(1)–N(1c)	101.35(9)
O(1b)–Mn(1)–O(1)	87.87(6)	O(2)–Mn(1)–N(1c)	86.73(7)
O(5a)–Mn(1)–O(1w)	93.82(8)	O(1)–Mn(2)–O(3d)	82.64(6)
O(1b)–Mn(1)–O(1w)	90.25(8)	O(1)–Mn(2)–O(3)	97.36(6)
O(1)–Mn(1)–O(1w)	88.02(8)	O(1)–Mn(2)–O(4e)	91.84(7)
O(5a)–Mn(1)–O(2)	91.82(7)	O(3)–Mn(2)–O(4e)	89.51(7)
O(1b)–Mn(1)–O(2)	84.01(7)	O(1)–Mn(2)–O(4a)	88.16(7)
O(1)–Mn(1)–O(2)	84.46(6)	O(3)–Mn(2)–O(4a)	90.49(7)
O(1w)–Mn(1)–O(2)	170.70(8)	Mn(1b)–O(1)–Mn(1)	92.13(6)
O(5a)–Mn(1)–N(1c)	82.28(7)	Mn(1b)–O(1)–Mn(2)	132.64(9)
O(1b)–Mn(1)–N(1c)	97.89(7)	Mn(1)–O(1)–Mn(2)	113.45(7)

Symmetry codes: For **1**: (a) $x-1/2, -y, z$; (b) $x-1/2, -y+1, z$; (c) $-x+3/2, y, z-1/2$; (d) $-x+3/2, y-1, z-1/2$.

For **2**: (a) $x+1, y, z$; (b) $-x+1, -y+1, -z$; (c) $-x, -y+1, -z+1$; (d) $-x+1, -y+2, -z$; (e) $-x, -y+2, -z$.

hydrothermal parameters, such as pH value, the temperature, reaction time, and molar ratio of the starting materials, may lead to quite different final products [12a]. Complexes **1** and **2** have not been successfully obtained under the conditions of hydrothermal synthesis used for the reported analog of Co [12a]. This result was related to the low stability of Mn^{2+} in basic aqueous solution and its relative ease of oxidation to higher valence manganese when the starting materials was mixed at ambient temperature in air under strong basic conditions, similar to the synthesis of $Mn(3,4\text{-pyda})(H_2O)$ and $Mn_3(OH)_2(SO_4)_2$ [11e,16]. However, experiment was performed in freshly boiled distilled water and a mild organic base, Et_3N , was adopted in place of sodium hydroxide, crystalline products of **1** and **2** were isolated. Interestingly, **1** and $[Mn(3,4\text{-pyda})(H_2O)]$ [11e] were prepared by using the same starting materials and hydrothermal parameters except for the reaction temperature. The latter can be obtained above 160 °C, while **1** was isolated at 175 °C. **2** was isolated as a single phase when the molar ratio of $Mn:3,4\text{-pyda}:Et_3N$ was changed from 1:1:2 (for **1**) to 1.5:1:3 (for **2**).

3.2. Crystal structures

3.2.1. Structure of $[M(3,4\text{-pyda})]$ (**1**)

1 crystallizes in orthorhombic with an asymmetric unit consisting of one formula unit and therefore there is only one metal environment. The Mn(II) atom is coordinated in a less common square pyramidal geometry [17] with a NO_4 donor set (Fig. 1a) coming from five different 3,4-pyda ligands. The Mn–O and Mn–N distances are 2.138(3)–2.159(3) and 2.225(4) Å, respectively. Each ligand is coordinated to five Mn(II) atoms through its two μ_2 -carboxylate groups and one pyridyl groups. The 3 position carboxylate acts in *syn,anti*-bridging mode, while the 4 position carboxylate in *syn,syn* mode, quite different from those (both in *syn,anti* mode) found in $Mn(3,4\text{-pyda})(H_2O)$ [11e]. The most interesting structural feature of **1** is the *syn,syn* carboxylates bridge the Mn(II) atoms into helical $Mn(\text{carboxylate})_2$ chains along *c*-axis, as shown in Fig. 2b. Each 3,4-pyda connects three helical chains

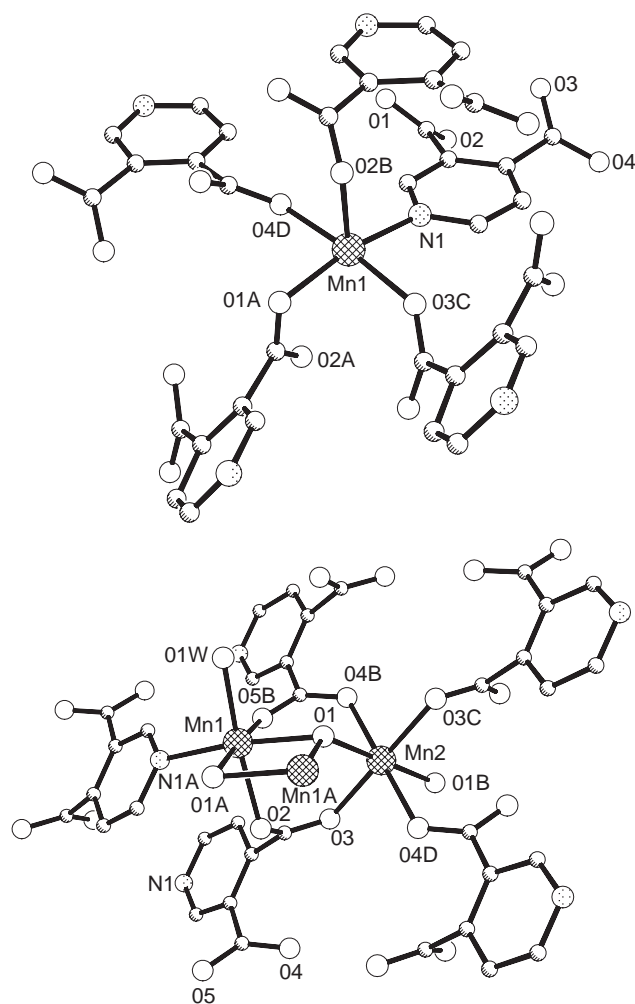


Fig. 1. Views of the local coordination geometries of the Mn atoms in the structures of **1** (a) and **2** (b).

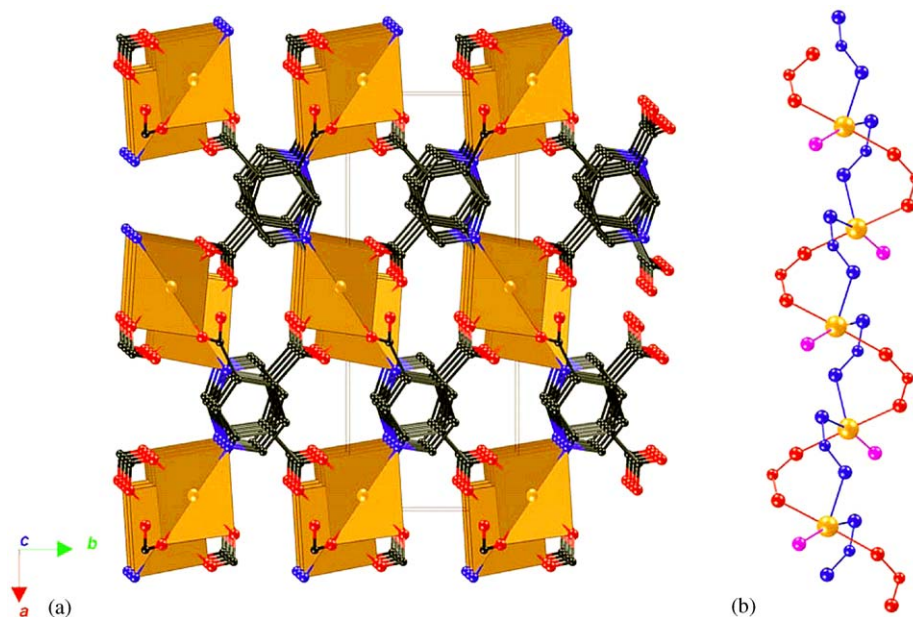


Fig. 2. Perspective views of the 3D coordination network (a) and the helical chain (b) in **1**.

via sharing its three functional bridging groups and each helical chain is linked with eight helical chains by sharing 3,4-pyda bridges, resulting in a 3D coordination structure (Fig. 2a). The intrachain Mn...Mn distance is 3.951 Å, significantly shorter than that (ca. 4.8 Å) found in Mn(3,4-pyda)(H₂O) [11e].

3.2.2. Structure of [Mn₃(OH)₂(3,4-pyda)₂(H₂O)₂]_n (**2**)

2 crystallizes in triclinic with an asymmetric unit consisting of half of formula unit and there are therefore two crystallographically independent Mn(II) atoms, Mn2 lies on an inversion centre where Mn1 are located on general position. The Mn1 atom is coordinated in an octahedral MnNO₅ geometry (Fig. 1b) to two carboxylate O atoms and one pyridyl N atom coming from three different 3,4-pyda ligands, two OH⁻ groups and one aqua molecules. The Mn1–O and Mn1–N bond lengths are 2.154(2)–2.204(2) and 2.285(2) Å, which are comparable with those found in Mn(3,4-pyda)(H₂O) [11e] and **1**, but significantly longer than those (2.066(2)–2.186(2) and 2.148(3) Å) of [Co₃(OH)₂(3,4-pyda)₂(H₂O)₂]_n [12a], which is dependent on sequence of their radius. The Mn2 atom is coordinated in an octahedral MnO₆ geometry with four carboxylate O atoms and two OH⁻ groups. The Mn2–O(hydroxy) and Mn2–O(carboxylate) bond lengths are 2.191(2) and 2.245(2)–2.2484(2) Å, respectively. Each 3,4-pyda ligand is coordinated to five metal atoms, and both carboxylate groups of each 3,4-pyda coordinate in *syn-anti* O,O'-bridging mode. Of marked interest us is that the whole structure is a 3D coordination network consisting of 1D Mn₃(OH)₂ chains and 3,4-pyda bridges (Fig. 3b). The

repeating trimeric structural unit in the metal hydroxide chain consists of two edge-sharing symmetry-related manganese octahedra (Mn1–Mn1) linked via μ₃-OH to a vertex of Mn2 octahedron (Fig. 3a). The Mn1–Mn1a, Mn1–Mn2 and Mn1a–Mn2 distances are 3.128(1), 3.659(2) and 3.982(2) nÅ, thus forming an irregular triangle. The Mn1–OH–Mn1a angle is 92.13(6)°, while Mn1–OH–Mn2 angles are 113.45(7)° and 132.64(9)°. Few structurally characterized compounds containing Mn(II) hydroxide units and polyfunctional ligands have been reported so far [16], and the bridging spacers were focused on dicarboxylate [16a,b] or inorganic anionic ligands [16c,d]. The present structure represents another new interesting example of 3D networks incorporating manganese hydroxide chains.

3.3. Magnetic properties

As illustrated in Fig. 4, the value of χ_MT for **1** is shown to be 4.00 cm³ mol⁻¹ K at room temperature per Mn^{II} ion, which is slightly smaller than that expected for the uncoupled Mn^{II} ion (*g* = 2.0, 4.38 cm³ mol⁻¹ K). Upon cooling, the value of μ_{eff} decreases very slowly and then abruptly below 40 K to reach 0.53 cm³ mol⁻¹ K at 2 K per Mn^{II} ion. The magnetic susceptibility above 30 K obeys the Curie–Weiss law with a Weiss constant θ of –9.15 K and a Curie constant *C* of 4.11 cm³ mol⁻¹ K, indicating the occurrence of a weak antiferromagnetic interaction between the Mn^{II} ions [11e].

The magnetic behaviours of **2** are displayed in Figs. 5–8. Phase purity of the bulk materials was confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study.

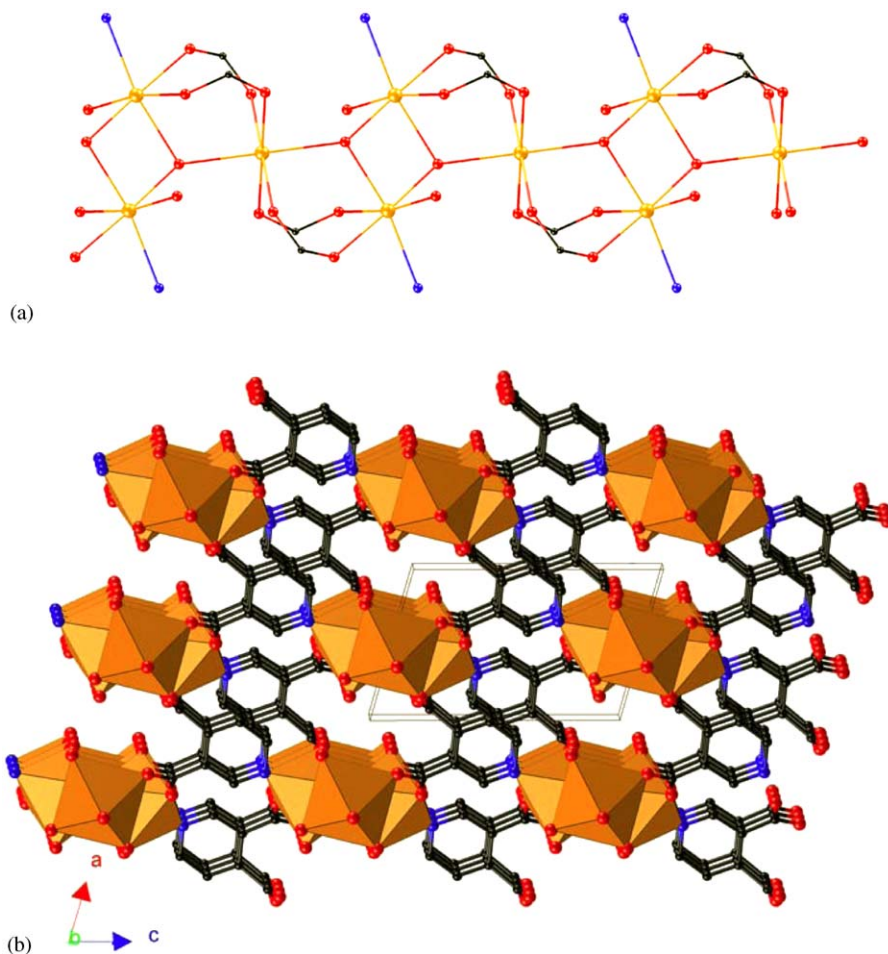


Fig. 3. Perspective views of the building unit of $\text{Mn}_3(\text{OH})_2$ chain (a) and the 3D coordination network (b) in **2**.

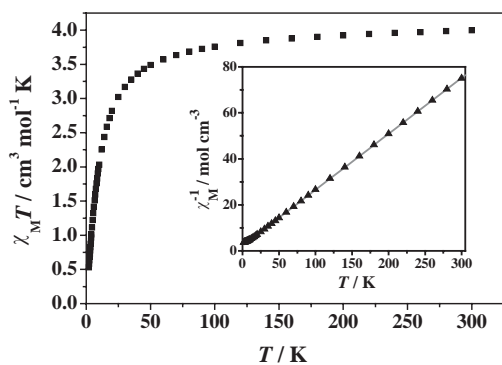


Fig. 4. Plots of $\chi_M T$ (7) (per Mn) and χ_M^{-1} (○) (inset) versus temperature for **1**.

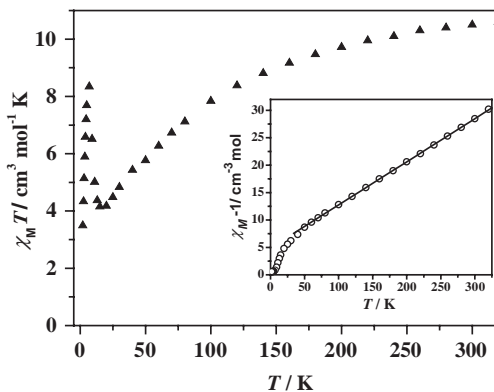
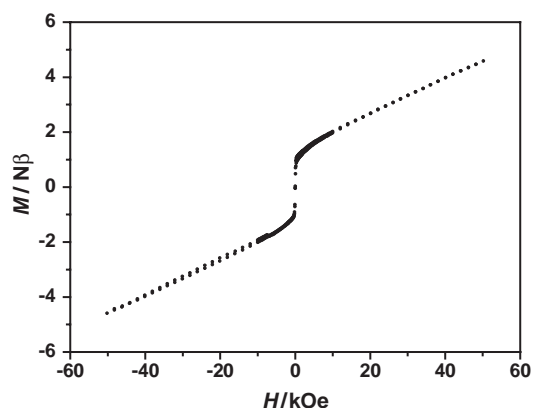
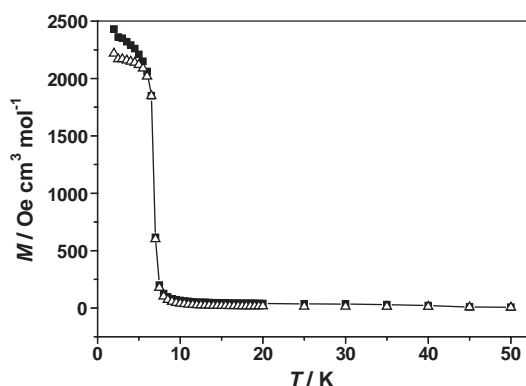
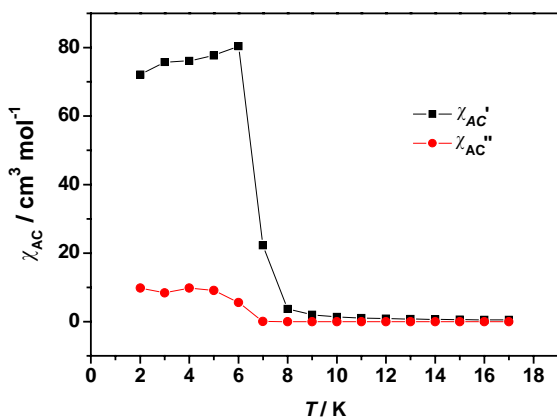


Fig. 5. Plots of $\chi_M T$ (7) (per Mn_3) and χ_M^{-1} (○) (inset) versus temperature for **2**.

For **2**, magnetic susceptibility data were measured with polycrystalline sample in 5.0 kOe field over the temperature range of 2–300 K (Fig. 5). $M(H)$ was measured from -50 to $+50$ kOe at 2 K the value of $\chi_M T$ at room temperature is $10.60 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ per Mn_3 unit.

Upon lowering temperature, a first decrease of the values of $\chi_M T$ is observed, a minimum ($4.13 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) is observed at 15 K. Below this minimum, $\chi_M T$ rapidly increases and reaches a very high value of $8.34 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 7 K. This curve is

Fig. 6. Field dependence of the magnetization at 2.0 K of **2**.Fig. 7. FCM (●) and ZFCM (△) data collected in an applied field of 10 Oe of **2**.Fig. 8. Temperature dependence of ac susceptibilities, in-phase (χ') and out-of-phase (χ'') measured on a polycrystalline sample of **2** at 1116 Hz (in zero applied dc field and 5 Oe oscillating ac field).

characteristic of ferrimagnetic behavior. The magnetic susceptibility obey the Curie–Weiss law above 50 K with a Weiss constant, $\theta = -61.63$ K, and a Curie constant,

$C = 12.69$ cm³ mol⁻¹ K, indicates a significant antiferromagnetic coupling between the Mn(II) $S = 5/2$ spins through the *syn-anti* carboxylato bridges. Considering the 1D manganese-hydroxide chain, the main competition interactions occur between two spin-up centres and one spin-down center, respectively from Mn polyhedra sharing edges ($d_{\text{Mn-Mn}} = 3.128(1)$ Å) and vertices ($d_{\text{Mn-Mn}} = 3.659(2)$ and $3.982(2)$ Å). The magnetic interactions between two metal ions in a polynuclear metal hydroxide cluster or in an extended magnetic lattice mainly depend on M–O–M angles. Ferromagnetic interaction for the M–O–M values close to 90° and antiferromagnetic for the large M–O–M angle is expected. For the edge-sharing manganese with Mn–OH–Mn bond angle of 92.13(6)°, a ferromagnetic superexchange is anticipated, whereas antiferromagnetic interactions should be favorable for the vertices connections with large angles of 113.45(7)° and 132.64(9)°, therefore, resulting in a ferrimagnetic behavior. The analogous phenomenon was recently documented in 3D coordination polymers containing 1D ferrimagnetic $\text{M}_3(\text{OH})_2$ chains ($M = \text{Co}^{\text{II}}$ or Ni^{II}) [7a,d,e]. A plot of the field-dependent magnetization measurement at 4 K is shown in Fig. 6. At the low field region, a sharp linear behavior from 0 to 7.0 kOe was observed. The $M(H)$ data then starts to reduce the slope and reaches a value of $4.6 \text{ N}\beta$ at 50 kOe, which saturation is not yet reached. A detected hysteresis loop was not observed at 4 K, indicating that **2** behaves as a soft magnet. The field-cooled and zero-field-cooled magnetization (FCM and ZFCM) curves of **2** measured in a low field of 50 Oe show an abrupt increase in M at ca. 7.0 K (Fig. 7) is characteristic of a magnetically ordered state below 7.0 K, in good agreement with the results of the ac magnetic susceptibilities. As shown in Fig. 8, in-phase ac magnetic susceptibility, χ' , exhibits a peak located around 7.0 K and out-of-phase ac susceptibility, χ'' , leaves from zero at 7.0 K. This behavior was found to be independent on the ac frequency used, indicating the presence of a 3D magnetic ordering at about 7.0 K.

4. Conclusions

Two new 3,4-pyridinedicarboxylate-bridged Mn(II) complexes have been synthesised under hydrothermal conditions. X-ray structural analysis shows **1** is a 3D coordination polymer incorporating helical Mn(carboxylate)₂ chain units and **2** is one 3D organo-inorganic coordination solid with 1D $\text{Mn}_3(\text{OH})_2$ chains. The 3,4-pyda ligands act as two different μ_5 -coordination modes in both complexes. Magnetic studies indicate the presence of 3D magnetic ordering at about 7.0 K in **2**.

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